Models for the Optical Properties of Clusters and Nanostructures

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1. Introduction

The electronic levels are quantized in atomic clusters and small nanostructures, essentially reflecting the behaviour of electrons in a potential well of finite size. The electronic properties are sensitive to the ordering of those electronic levels and to their evolution as the number of atoms in the cluster increases. The optical spectrum provides information on the electronic structure. In particular, the optical response of the clusters depends on their size and also on the cluster structure. This is an important feature, since the determination of the structure is, in general, a hard task, either using experimental techniques or sophisticated total energy calculations, and knowledge of the geometrical structure of a cluster is required as a basis for understanding many of its properties.

In this work we review some of the theoretical methods and models that are currently in use to calculate the response of clusters to general time-dependent external fields. One is often interested in the response to an external field that is not strong, and in such a case it is enough to consider linear response. For the simple case of a system with only one particle, the excited states can be calculated by solving the time-independent Schrödinger equation. Similarly, the probability $P_{if}(t)$ for transitions from an initial state $|\varphi_i\rangle$ to an excited state $|\varphi_f\rangle$ is calculated by solving the time-dependent Schrödinger equation in the presence of the time-dependent perturbing potential and then using the expression

$$P_{if}(t) = \left|\langle\varphi_f|\psi(t)\rangle\right|^2,$$

where $|\psi(t)\rangle$ is the solution of the time-dependent Schrödinger equation in the presence of the external field, with initial condition $|\varphi_i\rangle$ at $t = 0$. In the usual case of a many-electron system the whole method becomes very difficult because of the complications introduced by the interactions between the electrons. In this case, the process can be conveniently formulated within the framework of Density Functional Theory (DFT) [1], which has become the method most often used in the study of the electronic structure of molecules, nanostructures and solids. In particular, the spectrum of
optical excitations can be efficiently calculated by the so called Time Dependent Density Functional Theory (TDDFT) [2,3].

This paper presents a review of the theoretical methods used to study the optical spectrum of clusters and nanostructures based on the TDDFT. Before discussing that general method, the main theoretical concepts required to connect with the experiments are introduced in Section 2, and a simple approach based on the study of sum rules is presented in Section 3. The general formalism of the TDDFT is given in Section 4 and its formulation in the linear response regime in Section 5. Then Sections 6 to 9 present several practical ways that have been introduced to apply this formalism, with a first illustrative application to atoms. Sections 10 to 17 then provide abundant examples of the applications of TDDFT to the study of the optical excitations in clusters, mainly clusters of the metallic elements, and fullerenes. A recently developed method, based on the explicit solution of the time-dependent Kohn-Sham equations, is reviewed in Sections 18 and 19. This method is also able to treat nonlinear effects and this is one of its most interesting features. Some examples are shown in Section 20. Finally, in the last section of the paper, Section 21, a brief account of many-body techniques is presented.

2. Relation between theory and experiment

When a nanostructure interacts with an applied time-dependent electric field characterized by an external potential \( V_{\text{ext}}(\mathbf{r}, t) \), with Fourier components \( V_{\text{ext}}(\mathbf{r}, \omega) \) (we work in the longitudinal gauge)

\[
V_{\text{ext}}(\mathbf{r}, t) = \int d\omega \ e^{-i\omega t} V_{\text{ext}}(\mathbf{r}, \omega),
\]

the external field induces a time-dependent perturbation of the electron density \( \delta n(\mathbf{r}, t) \) (we neglect magnetic and current-induced effects)

\[
\delta n(\mathbf{r}, t) = \int d\omega \ e^{-i\omega t} \delta n(\mathbf{r}, \omega).
\]

The key quantity to calculate the response of the system in the linear regime is the dynamical susceptibility \( \chi(\mathbf{r}, \mathbf{r}', \omega) \), which relates the individual components of the induced density to those of the external potential, that is,
\[ \delta n(r, \omega) = \int d^3 r' \chi(r, r', \omega) V_{ext}(r', \omega). \] (4)

For the case of a dipole field, \( \delta n(r, \omega) \) allows to calculate the induced dipole moment. The dynamical polarizability \( \alpha(\omega) \), which is the ratio between the induced dipole moment and the intensity \( E_0 \) of the applied field, then becomes
\[ \alpha(\omega) = \frac{1}{E_0} \int d^3 r \delta n(r, \omega). \] (5)

Dissipation results in \( \delta n(r, \omega) \) being a complex function, and its imaginary part represents the power absorption of the cluster, that is due to electronic excitations. By application of the Fermi’s Golden Rule, one obtains the photoabsorption cross section
\[ \sigma(\omega) = \frac{4\pi\omega}{c} \text{Im} \alpha(\omega), \] (6)

where \( \text{Im} \alpha(\omega) \) is the imaginary part of the dynamical polarizability and \( c \) is the velocity of light.

Experiments have been performed to measure the photoabsorption spectrum, specially of metallic clusters. The typical experimental setup [4,5] is shown in Figure 1. A beam of neutral clusters is first produced in a cluster source by supersonic expansion of a vapor through a small nozzle. The beam is first collimated by a rectangular aperture and then photoionized by ultraviolet light (UV lamp in the Figure). The resulting cluster cations enter a quadrupole mass analyzer (QMA), and selected masses are steered into the detector. The entire cluster beam is illuminated by a collinear and counter-propagating laser beam. Upon absorption of light, the clusters warm up and fragment. The transverse recoil removes the daughter clusters away from the initial direction of motion of the collimated beam and the ratio between the number of clusters of a given size arriving at the detector with and without light excitation is proportional to the absorption cross section. One can adjust the QMA to a specific cluster mass and measure the counting rate of that cluster.

In the case of metallic clusters, the process responsible for the fragmentation is the excitation of a collective mode, the so called surface plasmon. All the valence electrons participate in this collective resonance, moving back and forth uniformly against the positive ionic background [6,7]. For Sodium clusters, for example, the excitation energy of the surface plasmon is about 3 eV. This energy is
higher than the binding energy of an atom in the aggregate, which is below 1 eV, and the excited cluster decays by evaporating single atoms. Using statistical models, the time required to evaporate an atom, if one assumes that the energy of the collective excitation is converted into atomic vibrations, turns out to be, for small clusters, orders of magnitude smaller than the time of flight of the molecular beam in the spectrometer. Consequently, it can be assumed that the photoabsorption and photofragmentation cross sections are equal. When the cluster size increases, the time required to evaporate atoms also increases and multiphoton absorption techniques have been used [6]. The surface plasmons in metallic clusters are similar to the giant dipole resonances in nuclei [8].

The integral of the photoabsorption cross section leads to the dipole sum rule (or Thomas-Reiche-Kuhn sum rule)

\[
\int \sigma(\omega) d\omega = 2\pi^2 \frac{e^2 \hbar^2}{m_e c} Z ,
\]

where \( e \) and \( m_e \) are the electron charge and mass respectively, \( \hbar \) is Planck’s constant divided by \( 2\pi \), and \( Z \) is the total number of electrons taking part in the collective motion. The experimental determination of \( \sigma(\omega) \) then helps identifying the collective nature of a resonance. The observed resonances of alkali clusters account for \( \approx 60\% \) of the total dipole strength.

For spherical metal particles of a diameter \( 2R \) small compared to the photon wavelength, the classical theory of the dynamical polarizability [9] gives the following expression for the photoabsorption cross section:

\[
\sigma(\omega) = \frac{4\pi Z e^2}{m_e c} \frac{\omega^2 \Gamma}{(\omega^2 - \omega_{\text{Mie}}^2)^2 + (\omega \Gamma)^2} ,
\]

where \( \omega_{\text{Mie}} \) and \( \Gamma \) represent the frequency and the width of the resonance, respectively. This relation assumes that all the dipole oscillator strength is exhausted by the surface plasma resonance at \( \omega_{\text{Mie}} \) (plasma-pole model). The frequency of the single dipole resonance, representing the collective oscillation of the valence electrons with respect to the positive ions, is related to the cluster radius by

\[
\omega_{\text{Mie}} = \frac{\sqrt{Z \hbar^4 c}}{m_e R^3} .
\]
This gives for $\omega_{\text{Mie}}$ a value equal the bulk plasma frequency $\omega_{\text{pl}}$ divided by $\sqrt{3}$ ($\omega_{\text{pl}} = \sqrt{\frac{4\pi e^2 n^0}{m_e}}$, where $n^0$ is the average electron density in the bulk).

3. Sum rules

The photoabsorption cross section is determined in equation (6) by the imaginary part of the polarizability tensor $\alpha(\omega)$. Alternatively [6], one can use the strength function $S(E)$

$$S(E) = \sum_n \delta(E - E_n) \langle n|Q|0\rangle^2,$$

(10)

connected to $\alpha(\omega)$ by

$$S(E) = -\frac{1}{\pi} \text{Im} \alpha(\omega).$$

(11)

In equation (10), the ket $|0\rangle$ represents the electronic ground state of the cluster and the sum $\sum_n$ is extended over the excited many-body states $|n\rangle$ of the system. $E_n$ are the excitation energies and $E = \hbar \omega$. The operator $Q$ represents the external field, the electric dipole operator in most cases of interest. The full response is not required in some applications, and a knowledge of some moments

$$m_k = \int dE E^k S(E),$$

(12)

of the strength function is sufficient to have a correct picture of the physical processes (in this equation $k$ is an integer number, positive or negative). For instance, the average energy $\bar{E}$ and the variance $\sigma^2$ of $\sigma(\omega)$ can be obtained from $m_0$, $m_1$ and $m_2$, as $\bar{E} = m_1/m_0$ and $\sigma^2 = m_2/m_0 - (m_1/m_0)^2$.

A direct evaluation of the moments $m_k$ is difficult, because the whole excitation spectrum is needed, but the odd moments can be easily obtained with RPA precision [6,10]. The RPA (Random Phase Approximation) [11], can be derived as the small amplitude limit of the time-dependent Hartree-Fock theory by linearizing the equations of motion. The characteristic feature of RPA is to construct excited states as a superposition of one particle-hole excitations. The linear moment $m_1$ for the electric dipole operator is model independent, and its RPA value
\[ m_1 = \frac{\hbar^2 e^2 Z}{2m_e} \tag{13} \]

is exact, so one obtains the sum rule of equation (7). By defining mean energies as \( e_k = (m_k/m_k.2)^{1/2} \), the bounds \( e_1 \leq E \leq e_3 \) and \( \alpha^2 \leq (e_3^2 - e_1^2)/4 \) can be proved. Also

\[ m_{-1} = \alpha / 2 \tag{14} \]

where \( \alpha \) is the static polarizability [12]. Consequently, one may estimate the centroid and variance of \( S(E) \) by evaluating the three RPA moments \( m_1 \), \( m_1 \) and \( m_3 \). The physical significance of the upper limit \( e_3 \) of \( E \) is that of a rapid oscillation (diabatic) of the valence electrons against the ions, whereas the lower limit \( e_1 \) is connected with a slow adiabatic motion of the electrons adjusting their density at any moment to the external field. This lower limit turns out to be a good estimation of the experimental energy of the collective excitation for metallic clusters [6,13]. The moment \( m_3 \) represents the restoring force parameter for the collective translational oscillations of the electrons against the ionic background [6]. For a spherically symmetric electron density \( n(r) \), \( m_3 \) is given by an overlap integral of the electronic and ionic densities [14]

\[ m_3 = e^4 \left( \frac{\hbar^2}{m} \right) \frac{4\pi}{3} \int n_+ (r) n(r) d^3r \tag{15} \]

This integral is easily evaluated for a metallic cluster of radius \( R \) in the spherical jellium model (SJM). In this model, the positive charge background of the ions is smeared out over the volume of the cluster, to form a distribution of positive charge with density

\[ n_+ (r) = n_+^0 \Theta(R - r) \tag{16} \]

where \( \Theta(R - r) \) is the step function, with values 1 for \( r < R \) and 0 for \( r > R \). The radius \( R \) of the positive background is related to the number of atoms, \( N \), in the cluster by the equation

\[ \frac{4}{3} \pi R^3 = N \Omega \tag{17} \]

where \( \Omega \) is the experimental volume per atom in the bulk metal. Also, the constant \( n_+^0 \) is related to \( \Omega \) and to the valence \( z \) (\( z = 1 \) for alkali elements) by

\[ z = n_+^0 \Omega \tag{18} \]
For the SJM, the moment \( m_3 \) becomes

\[
m_3 = \frac{\hbar^4 e^4 Z}{2m^2 r_s^3} \left( 1 - \frac{\delta Z}{Z} \right),
\]

(19)

where \( r_s \) is related to the average electron density \( n^0 \) of the bulk metal by

\[
r_s = \left( \frac{3}{4\pi n^0} \right)^{1/3}
\]

(20)

and \( \delta Z \) measures the spill-out of the electronic charge beyond the radius of the positive background

\[
\delta Z = 4\pi \int_0^\infty r^2 n(r) \, dr.
\]

(21)

By neglecting the spill-out charge, then \( 2m_1 = R^3 \) (the classical polarizability of a metallic sphere is \( \alpha = R^3 \)), and \( e_3 = \sqrt{\hbar^2 e^2 Z / m_k} \alpha = e_1 \) gives the resonance frequency of the classical Mie surface plasmon \( \omega_{\text{Mie}} \). In general, \( \bar{E} \) is a reasonable estimation for the resonance energy when most of the absorption strength is concentrated in a narrow region. This is the starting point of the plasmon-pole models. In those models \( e_1 = e_3 \) and the knowledge of the static polarizability determines the value of the dipolar plasma resonance energy as

\[
e_3 = \hbar \omega_{\text{pl}} \sqrt{\frac{1}{3} - \frac{\delta Z}{3Z}}.
\]

(22)

For \( \delta Z = 0 \), \( e_3 \) becomes equal to the classical Mie frequency \( \omega_{\text{Mie}} = \omega_{\text{pl}} / \sqrt{3} \).

Table I gives the calculated values of the bounds \( e_1 \) and \( e_3 \) of the dipole surface collective mode for some neutral and charged Na and K clusters [15]. LDA labels the results obtained using the local density approximation to exchange and correlation [1,16] in the calculation of the density and the single-particle orbitals needed in the RPA formulas for \( m_k \) and \( e_k \). On the other hand, NL corresponds to the results obtained using a nonlocal approximation, known as the Weighted Density Approximation (WDA) [17], that goes beyond the LDA (a brief description of the WDA is presented in Section 10). The experimental energies of the surface plasma resonance are in reasonable agreement with \( e_1 \), in particular for the NL approximation, and those experimental values are given in parenthesis next to the calculated \( e_3 \) (NL). The effect of the cluster charge is to increase the resonance
energy. The analysis of $e_1$ and $e_3$ for larger clusters shows that the resonance energy increases with size [15], a prediction in agreement with experiment [18]. The theory also allows to obtain an upper bound of the variance of the photoabsorption cross section, but the predicted widths of the resonances are, of course, larger than the experimental widths. The variance is found to decrease by charging the cluster.

The general expressions for the odd moments corresponding to $q$- and $l$- dependent external fields $j_l(qr)Y_{lm}(\theta,\phi)$ are given in ref. [14]. This field represents the angular decomposition of an incident photon, described as a plane wave $e^{i(qr-\omega t)}$. With those operators one can analyze the multipolar response and also the inelastic scattering of electrons (relevant for electron energy loss spectroscopy, EELS). In small metallic clusters, and for fields of high multipolarity, there is a competition between the coulombic contribution to the response (diffusivity and collective excitations) and the kinetic energy contribution (single-particle excitations). The later dominates for large $l$ or large momentum transfer $q$, indicating the vanishing of collective effects. The response of a metallic sphere to a photon of intermediate energy is dominated by dipolar excitations, and at large energies by electron-hole excitations [13,19,20]. As the size of the cluster increases, higher multipolar excitations start to dominate together with retardation effects (completely neglected until now).

4. Time Dependent Density Functional Theory. Formalism

The original formulation of the Hohenberg-Kohn-Sham Density Functional Theory [1,16,21,22] is an incomplete theory, so far as it is not in general applicable to excited states or to problems involving non-local potentials or time-dependent external fields, thus excluding the calculation of optical response properties, electronic spectra, quasiparticles, photochemistry, etc. However, theorems have now been proved for time-dependent Density Functional Theory (TDDFT) which extend the applicability of the original theory [23]. The first applications of TDDFT were actually done before its formal development and relied on the analogies with the time-dependent Hartree-Fock (TDHF) theory [24,25]. Techniques for avoiding summation over virtual states, typical of all perturbation methods, were developed and applied with success. This, together with the simple multiplicative form of the
DFT exchange-correlation potential makes easier the solution of the response equations. These methods are now used in all fields, ranging from atomic physics to nuclear physics to condensed matter physics, including applications to the study of the optical properties of clusters [23,26]. In this Section we introduce the foundations of TDDFT. A novel feature of this formalism, not present in ground-state DFT, is the dependence of the time-dependent density functionals on the initial many-body state. The main practical result of TDDFT is a set of time-dependent Kohn-Sham (TDKS) equations whose structure is similar to the time-dependent Hartree equations. However, the TDKS equations include, exactly in principle, all the many-body effects through an unknown, time-dependent local exchange-correlation potential.

Runge and Gross [27] have developed a theory for time-dependent potentials, similar to the Hohenberg-Kohn-Sham theory [21,22]. In a first theorem, a one-to-one mapping between time-dependent potentials and time-dependent densities that are $V$-representable (that is, densities that come from antisymmetric $N$-electron ground state wavefunctions for some choice of external potential $V(r,t)$) is proved. A second theorem proves an stationary-action principle. The proof of the first theorem is based on the evolution of a many-particle state $\Psi(t)$ under the influence of a potential $V(t)$, following the time-dependent Schrödinger equation. The initial state $\Psi(t_0) = \Psi_0$ is not required to be the ground state or some other eigenstate of the initial potential $V(r,t_0) = V_0$, and this means that the case of a sudden switching of the potential is properly included in the formalism. The time-dependent potentials are required to allow for a Taylor expansion around $t_0$. Then the first theorem can be formulated in the following way: The densities $n(r)$ and $n'(r)$ evolving from a common initial state $\Psi(t_0) = \Psi_0$ under the influence of two external potentials $V(r,t)$ and $V'(r,t)$, both Taylor-expandable, are always different provided that the potentials differ by more than a purely time-dependent ($r$-independent) function: $V(r,t) \neq V'(r,t) + c(t)$. By virtue of this theorem, the time-dependent density determines the external potential uniquely up to an additive, purely time-dependent function. On the other hand, the potential determines the time-dependent wave-function, which can be considered as a functional of the time-dependent density up to a purely time-dependent phase, that is
\[ \Psi(t) = e^{-iH(t)} \tilde{\Psi}[n](t) \].  As a consequence the expectation value of any quantum mechanical operator \( \hat{Q} \) is a unique functional of the density: \( Q[n](t) = \langle \tilde{\Psi}[n](t) | \hat{Q} | \tilde{\Psi}[n](t) \rangle \). In addition to their dependence on the density, these functionals depend on the initial state \( \Psi_0 \). Furthermore, the time-dependent particle and current densities can be calculated exactly from the following set of [hydrodynamical](https://en.wikipedia.org/wiki/Hydrodynamics) equations:

\[
\frac{\partial n(r,t)}{\partial t} = -\nabla \cdot \mathbf{j}(r,t) \tag{23}
\]

\[
\frac{\partial \mathbf{j}(r,t)}{\partial t} = -i \langle \Psi(t) \big| \hat{\mathbf{j}}(t) \big| \Psi(t) \rangle. \tag{24}
\]

The first equation stands from the continuity equation of quantum mechanics and the second from the quantum mechanical equation of motion of operators, where \( \hat{\mathbf{j}} \) is the usual paramagnetic current density operator

\[
\mathbf{j}(r) = \frac{1}{2i} \sum_{j=1}^{N} \left( \nabla_{r_j} \delta(r-r_j) + \delta(r-r_j) \nabla_{r_j} \right), \tag{25}
\]

and \( \hat{H}(t) \) is the Hamiltonian operator.

The second theorem deals with the variational principle of the action functional. From quantum mechanics we know that the time-dependent Schrödinger equation with the initial condition \( \Psi(t_0) = \Psi_0 \) corresponds to a stationary (not minimum) point of the quantum mechanical action integral

\[
A = \int_{t_0}^{t_f} dt \left\langle \Psi(t) \bigg| i \frac{\partial}{\partial t} \hat{H}(t) \bigg| \Psi(t) \right\rangle. \tag{26}
\]

From the previous one-to-one mapping between time-dependent potentials and densities, the action is a functional of the density \( A[n] \) that must have a stationary point at the correct time-dependent density. Thus the density can be obtained by solving the Euler equation
\[ \frac{\delta A[n]}{\delta n(r,t)} = 0 \quad (27) \]

with the appropriate boundary conditions. As in the static Hohenberg-Kohn formalism, one can write the action functional as

\[ A[n] = B[n] - \int_{t_0}^{t_f} dt \int d\mathbf{r} n(\mathbf{r},t)V(\mathbf{r},t) \quad (28) \]

with a universal ($\Psi_0$-dependent) functional $B[n]$ formally defined as

\[ B[n] = \int_{t_0}^{t_f} dt \left( \frac{\partial}{\partial t} - \hat{T} - \hat{U} \right) \left| \Psi(t) \right|^2, \quad (29) \]

where $\hat{T}$ is the kinetic energy operator and $\hat{U}$ is the operator for the Coulomb interaction between the electrons. The variational equation (27) and the hydrodynamical equations (23) and (24) are, of course, equivalent. The functionals $A[n]$ and $B[n]$ are in general unknown and well defined only for $V$-representable densities.

As in the static case, a time-dependent Kohn-Sham scheme can be introduced by considering a non-interacting system that reproduces the exact interacting density $n(\mathbf{r},t)$. Assuming the $V$-representability of the time-dependent densities we get the following time-dependent KS-equations:

\[ \left[ -\frac{\hbar^2}{2} \nabla^2 + V_{\text{H}}(\mathbf{r},t) + V_{\text{xc}}(\mathbf{r},t) + V(\mathbf{r},t) \right] \psi_i(\mathbf{r},t) = i \frac{\partial}{\partial t} \psi_i(\mathbf{r},t) \quad (30) \]

\[ n(\mathbf{r},t) = \sum_{i=1}^{N} |\psi_i(\mathbf{r},t)|^2. \quad (31) \]

In equation (30), $V(r,t) = V_N(r,t) + V_{\text{ext}}(r,t)$ is the sum of the nuclear (or ionic) potential $V_N(r,t)$ and the applied perturbing field $V_{\text{ext}}(r,t)$. The nuclei (or the ions) occupy positions $\mathbf{R}_k(t)$. On the other hand
\[ V_H(r,t) = \int \frac{n(r',t)}{|r-r'|} dr' \] is the time-dependent Hartree potential and \( V_{xc}(r,t) \) is the time-dependent exchange-correlation potential, that is defined through the equivalence between the interacting and fictitious non-interacting systems. As in the static case, the advantage of the time-dependent KS-scheme lies in its computational simplicity compared to other quantum-chemical schemes as the time-dependent Hartree-Fock or the configuration interaction (CI) methods.

5. Excitation energies in Time Dependent Density Functional Theory. Linear response

TDDFT has become the most popular method for the calculation of excitations in finite systems, both in physics (atomic, molecular and condensed matter) [2,3] and quantum chemistry. As a first approximation to the excitation energies, one can simply take differences \( \Delta \epsilon = \epsilon_f - \epsilon_i \) between the ground-state Kohn-Sham eigenvalues. Although this procedure is not entirely justifiable, it is often employed to obtain a first approximation to the excitation spectrum. It is well known that the Kohn-Sham eigenvalues and wave functions do not have a precise physical interpretation, with the exception of the eigenvalue of the highest occupied state, \( \epsilon_{\text{HOMO}} \), that is equal to minus the ionization potential \( IP \) of the system [28,29]. In addition, Chong et al [30] have shown that the orbital energies of other occupied levels of atoms and molecules can be interpreted as approximate, but rather accurate, relaxed vertical removal energies. It should be stressed that the relation \( \epsilon_{\text{HOMO}} = - IP \) and the findings of Chong et al [30] are valid in exact DFT, but not for the approximate exchange-correlation energy functionals currently used. Those relations fail for the LDA, but better functionals, specially those improving the asymptotic behavior of \( V_{xc} \), lead to more accurate results. An excellent agreement between the calculated Kohn-Sham energy eigenvalues and the experimental results for the removal energies of inner electrons of the noble gas atoms was obtained [31] using the nonlocal WDA approximation [17] (see Section 10). A similar good agreement was found [32] between WDA
eigenvalues of occupied orbitals of Sodium and Potassium clusters in the Spherical Jellium model and quasiparticle energies calculated by Saito et al [33] using the many-body GW formalism [3].

Another approach, called Δ-SCF (delta self-consistent field), is based on the observation that the Hohenberg-Kohn theorem and the Kohn-Sham scheme can be formulated for the lowest state of each symmetry class [34]. In fact, the single modification of the standard proofs is to restrict the variational principle to wave-functions of a specific symmetry. The unrestricted variation will clearly yield the ground-state. On the other hand, the states belonging to different symmetry classes will correspond to excited states. The excitations can then be calculated by simple total-energy differences. However, this approach suffers from two drawbacks: i) only the lowest lying excitation for each symmetry class is obtainable, and ii) the exchange-correlation (xc) functional that now enters the Kohn-Sham equations depends on the particular symmetry we have selected. As specific approximations for a symmetry dependent xc-functional are not available, one is forced to employ the usual ground-state functionals. The excitation energies calculated in this way are only of moderate quality.

TDDFT allows one to calculate the excited state energies of a many-body system based on information from an ordinary self-consistent DFT calculation. In the time-dependent approach, one studies the behaviour of the system subject to a time-dependent external perturbation. The response of the system is directly related to the \( N \)-particle excited states of the \( N \)-particle system. We now present the formalism developed by Petersilka et al [35] for a spin-unpolarised system. A formally exact Dyson-like representation of the linear density response of an interacting many electron system in terms of the non-interacting Kohn-Sham response is first derived.

The linear response \( \chi \) is a functional derivative

\[
\chi(r,t,r',t') = \frac{\delta n(r,t)}{\delta V_{ext}^\prime(r',t')}_{V_{ext}=0}
\]  

(32)
that measures the degree to which the density responds to the external perturbing potential in first order. \( \chi \) can also be viewed as the coefficient of the linear term in a functional power series of the time-dependent density in terms of \( V_{\text{ext}} \), that is,

\[
n(r, t) = n_0(r, t_0) + \int \int \chi(r, t, r', t') V_{\text{ext}}(r', t') \, dr' \, dt' + O(V_{\text{ext}}^2).
\]  

(33)

The linear response \( \chi_s \) of the fictitious non-interacting Kohn-Sham system is defined in a similar way

\[
\chi_s(r, t, r', t') = \frac{\delta n(r, t)}{\delta V_{\text{eff}}(r', t')} \bigg|_{V_{\text{ext}} = 0}
\]  

(34)

and can be computed exactly (see below). The effective potential \( V_{\text{eff}} \) corresponding to a given external potential \( V_{\text{ext}} \) is the time-dependent Kohn-Sham potential

\[
V_{\text{eff}}(r, t) = V_{\text{ext}}(r, t) + V_{\text{ex}}(r, t) + V_{\text{xc}}(r, t) + V_{\text{xc}}(r, t),
\]  

(35)

where all the components have been defined after equation (30). We now evaluate the following functional derivative

\[
\frac{\delta V_{\text{eff}}(r, t)}{\delta V_{\text{ext}}(r', t')} = \delta(r - r') \delta(t - t') + \int \int \int d\tau d\tau' \chi(r, t, r', t', \tau, \tau') \left[ \frac{\delta(t - t')}{|r - r'|} + K_{\text{xc}}[n_0](r, t, r', t') \right].
\]  

(36)

where

\[
K_{\text{xc}}[n_0](r, t, r', t') = \frac{\delta V_{\text{xc}}[n](r, t)}{\delta n(r', t')} \bigg|_{V_{\text{ext}} = 0}
\]  

(37)

is the so-called time-dependent exchange-correlation kernel (which is a functional of the initial ground-state density). Employing the chain rule for functional derivatives in equation (32) we have

\[
\chi(r, t, r', t') = \int \int \int d\tau d\tau' \frac{\delta n(r, t)}{\delta V_{\text{eff}}(r', t')} \frac{\delta V_{\text{eff}}(r', t')}{\delta V_{\text{ext}}(r, t')} \bigg|_{V_{\text{ext}} = 0}
\]  

(38)
and combining this with the previous equations we obtain the following Dyson-like equation for the interacting linear response in terms of the Kohn-Sham non-interacting response

\[
\chi(r,t,r',t') = \chi_s(r,t,r',t') + \int dr_1 dr_2 \chi_s(r_1,t_1,t_1) \left[ \frac{\delta(t_1 - t_2)}{|r_1 - r_2|} + K_{xc}[n_0](r_1,t_1,t_2,t_2) \right] \chi(r_2,t_2,r',t').
\]  

(39)

Taking the Fourier transform with respect to time, the exact frequency-dependent linear response function becomes

\[
\chi(r,r',\omega) = \chi_s(r,r',\omega) + \int dr_1 dr_2 \chi_s(r_1,\omega) K(r_1,r_2,\omega) \chi(r_2,r',\omega),
\]

(40)

where the Kernel \( K(r_1,r_2,\omega) \) is given by

\[
K(r_1,r_2,\omega) = \frac{1}{|r_1 - r_2|} + K_{xc}[n_0](r_1,r_2,\omega).
\]  

(41)

Equation (40) has to be solved iteratively. Multiplying now both sides of equation (39) with \( V_{ext}(r',t') \) and integrating over \( r' \) and \( t' \) yields

\[
n_1(r,t) = \int dr' \int dr' \chi_s(r,t,r',t') V_{eff}(r',t').
\]

(42)

where the notation \( n_1 \) has been chosen to explicitly indicate linear response. Fourier transforming with respect to time we have an exact representation

\[
n_1(r,\omega) = \int dr' \chi_s(r,r',\omega) V_{eff}(r',\omega) \equiv \int dr' \chi_s(r,r',\omega) V_{ext}(r',\omega) + \int dx K(r',x,\omega) n_1(x,\omega)
\]

(43)

showing that the exact linear density response of an interacting system, which can be directly used to compute the photoabsorption cross section (see equations (5) and (6)) , can be written as the linear density response on a non-interacting system to the effective perturbation \( V_{eff} \).
6. Techniques to study excitations in linear response. Matrix eigenvalue method

Let us consider the analytical structure of the interacting linear response function for a finite system. We now show that the linear response function has poles at $\omega = \Omega_m$, where $\Omega_m$ are the $N$-particle excitation energies of the actual system. Using the Kubo formula for the density response in terms of a retarded density-density correlation function [36]

$$\chi(r, t, r', 0) = -i\Theta(t)\left\langle 0 \left| \hat{n}(r, t) \hat{n}(r', 0) \right| 0 \right\rangle,$$

where $\Theta(t)$ is the step function, $\hat{n}(r, t)$ is the density operator and $|0\rangle$ is the exact many-particle ground state, and inserting a complete set of many-particle states $|m\rangle$, we have

$$\chi(r, t, r', 0) = -i\Theta(t)\sum_m \left\langle 0 | \hat{n}(r, t) | m \right\rangle \left\langle m | \hat{n}(r', 0) | 0 \right\rangle + i\Theta(t)\sum_m \left\langle 0 | \hat{n}(r', 0) | m \right\rangle \left\langle m | \hat{n}(r, t) | 0 \right\rangle.$$  

Notice that the density operator is particle-number conserving, that is, only connects $N$-particle excited states with the $N$-particle ground state. By taking into account the time-evolution of the density operator $\hat{n}(r, t) = e^{iHt} \hat{n}(r, 0) e^{-iHt}$ the linear response function can be rewritten as

$$\chi(r, t, r', 0) = -i\Theta(t)\left[ \sum_m A_m(r) A_m^*(r') e^{i(E_m - E_0)t} - \sum_m A_m^*(r) A_m(r') e^{-i(E_m - E_0)t} \right],$$

where $A_m(r) = \left\langle 0 | \hat{n}(r, t) | m \right\rangle$, and $E_m$ is the energy of the $m^{th}$ $N$-particle excited state. Fourier tranformation leads to the spectral representation

$$\chi(r, r', \omega) = \sum_m \frac{\left\langle 0 | \hat{n}(r) | m \right\rangle \left\langle m | \hat{n}(r') | 0 \right\rangle}{\hbar \omega - (E_m - E_0) + i\delta} = \sum_m \frac{\left\langle 0 | \hat{n}(r') | m \right\rangle \left\langle m | \hat{n}(r) | 0 \right\rangle}{\hbar \omega + (E_m - E_0) + i\delta}.$$
One can observe that the time-Fourier transformation of the linear response function has poles at
\( \hbar \omega = \pm (E_m - E_0) \), that is, at the excitation energies of the \( N \)-particle system. We have seen previously that the interpretation of the Kohn-Sham single-particle energy differences as excitation energies has no rigorous basis and that in practical implementations they may differ substantially from the experimental excitation energies.

In the work of Petersilka et al [35] excitation energies are extracted from TDDFT by exploiting the fact that the frequency-dependent linear density response of a finite system has discrete poles at the excitation energies of the unperturbed system. The non-interacting susceptibility, which is needed to solve equation (40), can be computed directly form the Kubo formula and has the form

\[
\chi_s(r, r', \omega) = \sum_{k, j} \left( f_j - f_k \right) \frac{\psi^*_k(r) \psi_j(r) \psi^*_j(r') \psi_k(r')}{\hbar (\omega - \omega_{kj}) + i\delta} \tag{48}
\]

where \( \hbar \omega_{kj} = \epsilon_j - \epsilon_k \) and \( f_j \) are the Fermi occupation numbers of the \( j \)th single-particle orbitals obtained from the Kohn-Sham calculation. As a function of \( \omega \), \( \chi_s \) has poles at the Kohn-Sham orbital energy differences \( \omega_{kj} \). In order to calculate the shift towards the true excitation energy \( \Omega \), we rewrite equation (43) for the induced density as

\[
\int dr \delta (r - x) - \int dr' \chi_s(r, r', \omega) K(r', x, \omega) \right) n_1(x, \omega) = \int dr' \chi_s(r, r', \omega) V_{ext}(r', \omega) \tag{49}
\]

where we see that the integral operator acting on \( n_1 \) on the left-hand side cannot be invertible for \( \omega \to \Omega \), because if it was invertible we can act with the inverse operator and get on the right-hand side a finite value, in contradiction with the fact that \( n_1 \) has poles at the excitation energies. Thus, the true excitation energies \( \Omega \) can be characterized as those frequencies where the eigenvalues of this integral operator vanish. As noted previously, in the limit \( \omega \to \Omega \) the linear density \( n_1 \) has a pole, while the right-hand side of equation (49) remains finite. For the equality to hold, it is therefore required that the operator acting on \( n_1 \) on the left hand side of (49) has zero eigenvalues at the
excitation energies $\Omega$, i.e. $\lambda(\omega) \to 1$, when $\omega \to \Omega$, where $\lambda(\omega)$ is the solution of the eigenvalue equation

$$
\int dr^* \int dr^* \chi_n(r, r^*, \omega) \left[ \frac{1}{|r^* - r|} + K_{xc}\left[n_0\right](r^*, r, \omega) \right] \xi(r', \omega) = \lambda(\omega) \xi(r, \omega).
$$

(50)

This is a rigorous statement that allows the determination of the excitation energies from the knowledge of the independent-particle Kohn-Sham $\chi_n$ and the kernel $K_{xc}$. It is possible to transform this equation into another eigenvalue equation having the true excitation energies $\Omega$ as eigenvalues [37]. We begin by defining the quantity

$$
\zeta_{jk}(\omega) = \int dr dr^* \psi_j^*(r) \psi_k^*(r) \left[ \frac{1}{|r^* - r|} + K_{xc}\left[n_0\right](r^*, r, \omega) \right] \xi(r', \omega).
$$

(51)

With the help of $\zeta_{jk}$, equation (50) can be written in the form

$$
\sum_{jk} \left( f_k - f_j \right) \psi_j^*(r) \psi_k^*(r) \zeta_{jk}(\omega) = \lambda(\omega) \xi(r, \omega).
$$

(52)

By solving this equation for $\xi(r, \omega)$ and inserting the result into (51) we arrive at the equation

$$
\sum_{jk} \left( f_k - f_j \right) M_{jk, j'k'} \zeta_{j'k'}(\omega) = \lambda(\omega) \zeta_{jk}(\omega)
$$

(53)

where the coupling-matrix element is defined

$$
M_{jk, j'k'}(\omega) = \int dr dr' \psi_j^*(r) \psi_k(r) \psi_j^*(r') \psi_k(r') \left[ \frac{1}{|r - r'|} + K_{xc}\left[n_0\right](r, r', \omega) \right].
$$

(54)

Introducing now the new eigenvector
\[ \beta_{jk} = \frac{\zeta_{jk}(\Omega)}{\Omega - (\varepsilon_j - \varepsilon_k)}, \]  

Taking the \( \eta \rightarrow 0 \) limit, and using the condition \( \lambda(\Omega) = 1 \), it is straightforward to recast (53) into the eigenvalue equation

\[ \sum_{jk} \left[ \delta_{jj'} \delta_{kk'} (\varepsilon_j - \varepsilon_{k'}) + (f_{j'} - f_j) M_{jk,j'k'}(\Omega) \right] \beta_{jk'} = \Omega \beta_{jk}. \]  

The exact solution of this equation fully incorporates the collective electronic excitations. To solve the eigenvalue equation (53) one can expand all quantities in an appropriate basis and solve numerically the resulting matrix-eigenvalue equation. An alternative way to calculate \( \Omega \) is to expand all quantities appearing in eq. (50) about one particular energy difference \( \Delta \varepsilon = \varepsilon_j - \varepsilon_k \) between the Kohn-Sham eigenvalues of the occupied orbital \( k \) and the unoccupied orbital \( j \). Assuming that the true excitation energy is not far away from \( \Delta \varepsilon \), it is sufficient to consider only the lowest order terms in those expansions. This leads to

\[ \Omega_{jk} = (\varepsilon_j - \varepsilon_k) + B(\Delta \varepsilon). \]  

\( B(\Delta \varepsilon) \) is a correction given by

\[ B(\Delta \varepsilon) = 2R \int drdr' \psi_j^*(r) \psi_j(r') \psi_k^*(r') \psi_k(r) \left[ \frac{1}{|r - r'|} + K_{xc}[n_0](r, r', \Delta \varepsilon) \right], \]  

where \( R \) indicates the real part of the expression. Equations (57) and (58) provide a simple and fast way to calculate excitations energies, although this method is not as precise as solving directly equation (56). The approximation can be viewed as an attempt to correct the Kohn-Sham excitation energies individually without including collective electronic effects. Apart from the truncation of the expansions, two main approximations are necessary: (i) the static Kohn-Sham orbitals have to be
calculated with an approximate static exchange-correlation potential \( V_{xc}(\mathbf{r}) \), and (ii) the frequency-dependent exchange-correlation kernel \( K_{u\alpha}(\mathbf{r}, \mathbf{r}', \omega) \) has to be approximated.

It is also possible to derive an operator whose eigenvalues are the square of the excitation energies, reducing then the dimensions of the matrix equation (56) \([38,39]\). The oscillator strengths can then be obtained from the eigenfunctions of that operator

\[
\left( \omega^2_{jk\sigma} \delta_{jj} \delta_{kk} \delta_{\sigma\tau} + 2\sqrt{f_{jk\sigma}} \omega_{jk\sigma} M_{jk\sigma,j'k'\tau} \sqrt{f_{jk'\tau}} \omega_{jk'\tau} \right) \mathbf{F}_n = \Omega^2_{n} \mathbf{F}_n .
\] (59)

Here \( \sigma \) is the spin index, \( \omega_{jk\sigma} = \epsilon_{jk\sigma} - \epsilon_{jk'\tau} \) are the Kohn-Sham transition energies, and \( f_{jk\sigma} \) are the differences between the occupations of the \( j \) and \( k \) states. The coupling matrix \( M_{jk\sigma,j'k'\tau} \) is the generalization of \( M_{jk,j'k'} \) of equation (54) to the spin-dependent case. Some simplifications can also be introduced to solve approximately this equation \([39]\). Let us consider the spin unpolarized case, i.e., \( f_{jk\uparrow, \downarrow} = f_{jk\downarrow, \uparrow} = f_{jk} \) (the results can be easily generalized to any spin configuration). Assuming that the coupling between different one-electron transitions is weak, one can neglect all matrix elements with \( j \neq j' \) and \( k \neq k' \). The only remaining off-diagonal elements of the coupling matrix are generated by the spin index, and equation (59) reduces to a series of independent \( 2 \times 2 \) matrix equations. Solving for the transition energies,

\[
\Omega_{jk} \approx \left( \omega_{jk} + 2f_{jk} \left( M_{jk\uparrow, jk\uparrow} \pm M_{jk\uparrow, jk\downarrow} \right) \right)^{1/2} .
\] (60)

The plus sign describes transitions to the singlet excited state and the minus corresponds to triplet transitions. The approximation can again be viewed as an attempt to correct the Kohn-Sham excitation energies individually without including collective electronic effects. Assuming that the corrections with respect to the Kohn-Sham transition energies are small, one arrives at a further simplification by taking a linear expansion around \( \omega_{jk} \)

\[
\Omega_{jk} \approx \left( \epsilon_{j} - \epsilon_{k} \right) + f_{jk} \left( M_{jk\uparrow, jk\uparrow} \pm M_{jk\uparrow, jk\downarrow} \right) ,
\] (61)
This equation is equivalent to the result in eq. (57).

7. The exchange-correlation kernel

As we have seen in the previous sections, a main ingredient in linear response theory is the exchange-correlation kernel \( K_{xc} [n_0](\mathbf{r}, \mathbf{r}', \omega) \). This is a complex quantity that includes all non-trivial many-body effects. Approximate kernels have been proposed over the past years and we consider here some of the most commonly used ones. The simplest and most used one is the ALDA (adiabatic local density approximation) kernel [40]

\[
K^{ALDA}_{xc} [n](\mathbf{r}, t, \mathbf{r}', t') = \delta(\mathbf{r} - \mathbf{r}')\delta(t - t')K^{LDA}_{xc} [n_{\text{hom}}(\mathbf{r}, t)]
\]

where

\[
K^{LDA}_{xc} [n] = \frac{dV^{LDA}_{xc} [n](\mathbf{r})}{dn}
\]

is just the derivative of the exchange-correlation potential of a homogeneous electron gas with density \( n \), that is, \( V^{LDA}_{xc} [n](\mathbf{r}) = \frac{\partial E^{\text{hom}}_{xc} [n]}{\partial n(\mathbf{r})} \). The ALDA kernel is local both in the space and time coordinates.

Another exchange-correlation kernel was derived by Petersilka et al [35]. Its derivation starts from a simple analytic approximation to the exchange-only optimized effective potential (OEP) [41,42]. The OEP kernel has the following form

\[
K^{OEP}_{xc} (\mathbf{r}, t, \mathbf{r}', t) = -\delta(t - t') \frac{1}{2} \frac{\left| \sum_{\mathbf{k}} \psi^*_k (\mathbf{r}) \psi_k (\mathbf{r}') \right|^2}{n(\mathbf{r})n(\mathbf{r}')}. \]


As in the ALDA case, the OEP kernel is local in time. It should be noticed that in the calculation of excitation energies through equations (57) and (58) using the ALDA or the OEP kernels, only ground state quantities are needed, that is, Kohn-Sham orbitals and energy eigenvalues.

Recently, Görling and coworkers have derived and implemented the exact-exchange kernel (EXX) for solids [43]. Using the EXX, Kurth and Von Barth [44] have computed the electronic excitations for atoms obtaining good agreement with experiment, and their results are encouraging for the development of new kernels having exact-exchange as an ingredient. A simplified version of the EXX scheme has been applied to clusters and will be reviewed in Section 19 below.

8. Application of linear response theory to atoms

The lowest excitation energies of atoms of the alkaline earth and the zinc groups, calculated from equations (56) and (57), are given in Table 2 [35,39]. The LDA columns report results obtained with the LDA exchange-correlation potential and the ALDA kernel. On the other hand the OEP columns correspond to the use of the OEP potential and the OEP kernel. First of all, the Table shows how the difference $\Delta \epsilon$ of energy eigenvalues is corrected by the term in eq. (58), leading to improved excitation energies $\Omega_{\text{approx}}$. The OEP values $\Omega_{\text{approx}}^{\text{OEP}}$ are superior to the LDA results $\Omega_{\text{approx}}^{\text{LDA}}$, and also better than the $\Delta_{\text{SCF}}$ values. The $\Delta_{\text{SCF}}$ results are obtained by subtracting the total energies corresponding to the ground state and excited configurations. Petersilka et al [35] have argued that the main reason for the superiority of the OEP potential is that it is self-interaction free, and therefore has the correct asymptotic $-1/r$ behaviour far from the nucleus, while the LDA exchange-correlation potential decays exponentially. From this argument, the importance of a good description of the static exchange-correlation potential becomes evident. A study of the excitation energies of the CO molecule [46] indicates again a good agreement with experiment.

However, Chelikowsky and coworkers [39] have pointed out that the differences between $\Omega_{\text{approx}}^{\text{LDA}}$ and the experimental excitation energies are due to the approximations involved in equations (57) and
When the excitation energies are calculated by exactly solving eq. (56) (the results are given in the column $\Omega^\text{exact}_{\text{LDA}}$ of Table 2) the experimental and theoretical results agree within 5% - 10% for all atoms. The differences between $\Omega^\text{exact}_{\text{LDA}}$ and $\Omega^\text{approx}_{\text{LDA}}$ show the important role of collective electronic effects. The electronic correlations are particularly large for Zn and Cd, being caused by $d$ levels which are close in energy. The encouraging conclusion is that the wrong asymptotic behaviour of the LDA potential appears not to be as important for the excited state properties as previously thought [35,47], but more work needs to be done to clarify this point. Table 3 presents the calculated singlet $^1S \rightarrow ^1P$ and triplet $^1S \rightarrow ^3P$ transition energies for the same atoms [39]. The TDLDA transition energies are in better agreement with experiment than the results obtained by the OEP or $\Delta_{\text{SCF}}$ methods. Although the singlet excitation energies from the OEP method are almost as accurate as the TDLDA energies, the triplet transition energies are less accurate, because the OEP method does not include coulomb correlation effects, which play a significant role for triplets.

### 9. Selfconsistent Green´s Function Method

There is another traditional method [24,25] to calculate the excitations in linear response by self-consistently solving equation (43): this requires the evaluation of the independent-particle susceptibility $\chi_s$, given by equation (48). This expression involves an explicit sum over the complete energy eigenvalue spectrum of the LDA effective potential $V_{\text{eff}}$. That is, not only the occupied orbitals are required, but also the unoccupied bound states and the continuum orbitals as well. This problem can be circumvented by using the Green’s function associated to the LDA Schrödinger-type equation

$$\left[ E + \frac{1}{2} \nabla^2 - V_{\text{eff}}(r) \right] G(r, r'; E) = \delta(r - r').$$  \hspace{1cm} (65)

$G(r, r'; E)$ has an eigenfunction expansion
\[ G(r, r', E) = \sum_m \frac{\psi_m^+(r)\psi_m(r')}{E - \epsilon_m \pm i\delta} \]  

(66)

and satisfies the symmetry condition

\[ G(r, r'; E) = G^*(r', r; E) . \]  

(67)

Using the Green functions, the expression for the susceptibility \( \chi \) becomes [24,25]

\[ \chi_s(r, r', \omega) = \sum_{k=1}^{\text{occ}} \left[ \psi_k^+(r)\psi_k^*(r')G(r, r'; \epsilon_k + \hbar\omega) + \psi_k(r)\psi_k(r')G^*(r, r'; \epsilon_k - \hbar\omega) \right] \]  

(68)

where the sum is now restricted to occupied states. The integral equation (43) is then solved iteratively. If the result of the first iteration is inserted into equation (5) we obtain the independent particle approximation to \( \alpha(\omega) \). The photoabsorption cross section is then calculated from eq. (6).

10. Application of linear response theory to metal clusters.

Spherical Jellium model

The linear response theory can be applied to study the response of atomic clusters to a laser pulse of wavelength in the optical range. The TDLDA, in conjunction with the jellium model (see Section 3), follows the Mie result of eq. (8) in a qualitative way, shown schematically in Figure 2 for the case of Sodium clusters [6]. The dipole absorption cross section of spherical Sodium clusters usually exhibits a dominant peak, which exhausts 75-90 % of the dipole sum rule, and is shifted by 10-20 % with respect to the Mie frequency. The centroid of the strength distribution tends towards the Mie resonance in the limit of a large metallic sphere. Its red shift in finite clusters is a quantum mechanical, finite size effect, closely related to the spill-out of the electrons beyond the edge of the positive jellium background. On the other hand, about 10-25 % of the dipole strength is typically found at higher energies, and can be interpreted as a reminiscence of a strongly fragmented volume...
plasmon. Often, the dominant peak is fragmented into two or more lines. For spherical clusters this can be attributed to the interference of specific particle-hole excitations (or more complicated ones) with the predominant collective mode. This fragmentation may be compared to the Landau damping in a solid.

Before presenting specific applications, it is convenient to recall the main features of the electronic structure of clusters of the alkali metals. The population in the typical experiments in which the clusters form by aggregation of atoms in a supersaturated vapor, shows magic sizes corresponding to a number of atoms \( N = 2, 8, 18, 20, 34, 40 \ldots \) [48]. These magic numbers are explained by the formation of electronic shells in the common self-consistent potential of the cluster, that to a good approximation can be considered as a spherical droplet. The effective potential can be modeled by using the spherical jellium model. Then, as the cluster grows in size, the electronic shells become filled in the order \( 1s, 1p, 1d, 2s, 1f, 2p \ldots \). Clusters with filled electronic shells show an energy gap between the highest occupied and the lowest unoccupied molecular orbitals (HOMO-LUMO gap), and are evidently more stable than other clusters, giving rise to the observed magic numbers.

Most of the specific calculations to be reviewed next, and up to Section 16 included, use the Green’s function method. However, when other techniques, like the matrix eigenvalue method, are used, this will be explicitly indicated. The results of a TDLDA calculation [26,49] of the photoabsorption spectrum for Na\(_{20}\) within the spherical jellium model are shown in Figure 3. The dotted curve is the spectrum obtained using the independent-particle susceptibility \( \chi \), in equations (4) or (33), and the continuous line is the result for the interacting susceptibility \( \chi \). The ground state electronic configuration of Na\(_{20}\) in the spherical jellium model is \( 1s^2\ 1p^6\ 1d^{10}\ 2s^2 \), where the superscripts indicate the occupation of the electronic shells. Above these occupied subshells there are other unoccupied ones \( 1f, 2p, 1g, 2d, 3s \ldots \) and the peaks in the noninteracting spectrum represent allowed particle-hole excitations in which one electron is promoted from an occupied level to an unoccupied one. The transitions have been artificially broadened to simulate the effect of temperature (a full discussion of temperature effects is presented in Section 17). When electron-electron
interactions are switched on (using the fully interacting χ) some particle-hole transitions are shifted in energy, just as equation (58) indicates, and other excitations lose their individual identities, merging into a collective resonance.

Compared to experiment, the LDA calculations for the spherical jellium model [6,49] yield an insufficient red shift of the collective Mie resonance. For instance, Yannouleas et al [50] predicted the plasmon position of Na₁₈ at 2.82 eV, to be compared with the peak experimentally observed at 2.53 eV [51]. This is also evident for Na₂₀ in Figure 4, where the calculated resonance lines [26] have been broadened to simulate finite temperature effects [6,52]. The form of the LDA spectrum is similar to the experimental one [53], but the main LDA peak is displaced 0.3 eV to higher energy. The physical process underlying the fragmentation of the spectrum of Na₂₀ is, however, not well described by the LDA. In the LDA calculation, fragmentation occurs because of the proximity to the plasmon line of a particle-hole excitation ($2s \rightarrow 3p$) with energy $\hbar \omega = 2.8$ eV. In addition, the $3p$ subshell is practically degenerate with the vacuum level, and the fragmented line is broadened by the proximity of transitions from the $2s$ states to scattering states in the energy continuum. In contrast, the experimental ionization threshold lies at an energy of 3.76 eV, more than 1 eV higher than the main plasmon peak. A calculation using a spherical jellium with a smoothed surface leads to an improvement of the position of the dipole resonance [54].

Replacing the LDA by a nonlocal description of exchange and correlation improves the results. Calculations [49] using the nonlocal Weighted Density approximation (WDA) [55] (the continuous line in Figure 4) shift the plasmon resonance to lower energies, and place the main peak at 2.56 eV. This effect arises from a better description of the asymptotic (large r) behaviour of the exchange-correlation potential $V_{xc}$ and from the improvement of the local field correction, or kernel $K_{xc}$, with respect to the LDA. In the WDA, the exchange-correlation hole around an electron at position $r_1$

\[ n_{xc}(r_1, r_2) = n(r_2) \left[ g_{xc}(r_1, r_2) - 1 \right] \]  

presents two improvements with respect to the LDA. One is that the prefactor $n(r_2)$ is not approximated by the local density $n(r_1)$. In the LDA, the pair correlation function $g_{xc}(r_1, r_2)$ is replaced by $g^h_{xc}(r_1 - r_2, n(r_1))$, that is, the pair-correlation function for a homogeneous ($h$) electron
gas with density $n$ equal to the local density $n(r_1)$. In the WDA, the functional form $g_{sc}^h(\mathbf{r}_1 - \mathbf{r}_2; n)$ for a homogeneous electron gas is preserved, but the effective density $n = \tilde{n}(r_1)$ is fixed at each point $r_1$ by requiring the fulfillment of a sum rule stating that the integral of $n_{sc}(r_1, r_2)$ over the variable $r_2$ equals the exact value of $-1$. This means that the effect of the exchange-correlation hole is equivalent to removing a net charge of one electron from the neighborhood of the reference electron. The WDA prescription leads to an improved potential $V_{sc}^{WDA}$ and kernel $K_{sc}^{WDA}$. Returning to Na$_{20}$, the more accurate $V_{sc}^{WDA}$ also leads to an improved value of the ionization threshold, 3.27 eV, which does not interact with the plasmon because of the large separation between those two features. Instead, a shoulder develops at $\approx 2.7-2.8$ eV, and a pronounced secondary peak appears on the low energy side of the resonance, at $\approx 2.2$ eV, both features being due to the interaction of the plasmon with particle-hole excitations. Three resonances observed [56] at $\approx 2.19$, 2.41 and 2.76 eV, support the predicted WDA spectrum in the region below 2.9 eV. Calculations including self-interaction corrections (SIC) [57,58] also improve the results with respect to the LDA. SIC corrects for the spurious self-interaction of an electron with itself and improves the asymptotic behaviour of $V_{sc}$. Saito et al [57] introduced SIC corrections in the kernel $K_{sc}(n)(\mathbf{r}, \mathbf{r}')$ by an Amaldi-type correction

$$K_{sc}^{SIC}(r_1, r_2) = \frac{N - 1}{N} K_{sc}^{LDA}(r_1, r_2),$$

where $N$ is the number of electrons. On the other hand, Pacheco and Ekardt [58] followed the standard SIC scheme.

Interesting effects are expected when the plasmon excitation energy is close to the ionization threshold. This occurs for large cluster anions [49,59]. For small negatively charged clusters, the electron detachment threshold is low, and the energy of the collective resonance lies in the region of electronic excitations to the continuum of states, where Landau damping produces a broadening of the resonance. This is appreciated by comparing the calculated spectrum of Na$_{19}$, given in Figure 5, with that for neutral Na$_{20}$ in Figure 4 (the two clusters are isoelectronic, with 20 electrons). The WDA was also used in the calculations reported in Figure 5. The electron detachment threshold of Na$_{19}$ is
indicated by the arrow in Figure 5. As the cluster size increases, the plasmon approaches the region of
discrete states. Then, when the detachment threshold of the negative cluster lies in the region of the
plasmon resonance, electron emission becomes a decay mechanism which competes with the usual one of evaporation of atoms. The calculated photoabsorption cross sections of $\text{Na}^{-91}$ and $\text{Na}^{-197}$ are
also given in Figure 5. In those two clusters, the detachment threshold overlaps with the collective
resonance. Reiners and Haberland [60] measured the photoabsorption cross section of $\text{Na}^{-91}$ and
have found a broad collective resonance centered at 2.65 eV (its width is 0.92 eV), whose decay can lead to two final channels: atom and electron emission. The calculated position of the collective resonance of $\text{Na}^{-91}$ in Fig. 5 is 2.69 eV, in good agreement with the experiment of Reiners and Haberland. Changing the net cluster charge, from anionic to neutral to cationic clusters, for a fixed total number of valence electrons, has the effect of shifting slightly the plasmon to higher energies. For instance, the maximum of the resonance occurs at 2.65 eV and 2.77 eV for $\text{Na}^{-91}$ and $\text{Na}^{+93}$ respectively, and the corresponding width decreases from 0.92 eV to 0.51 eV.

11. Shape deformations. Role in the absorption spectrum

A splitting of the collective resonance is observed in clusters with open electronic shells, which is a consequence of the static spheroidal deformations of the cluster shape. A double peak in the photoabsorption cross section has been observed for K and Na clusters [4,61,62] and for Ag clusters in the region $10 \leq N \leq 16$ [63]. The two modes correspond to excitations along the main axis of the spheroid and perpendicular to that axis, respectively. Figure 6 shows the experimental results of Borggreen et al [62] for cationic Na clusters. These results reveal the systematics of cluster shapes after the spherical clusters with 8 and 20 electrons, respectively. The trend in the shapes goes: spherical $\rightarrow$ prolate $\rightarrow$ oblate $\rightarrow$ spherical. This systematics is reproduced by total energy calculations within a spheroidal jellium model [64], and the splitting of the collective resonance is obtained by the TDLDA applied to the deformed clusters [65]. In larger clusters, it is difficult to disentangle the
effects originating from static shape deformations from those due to the fragmentation mechanism discussed above.

A splitting of the dipole resonance into three peaks has been observed in some Na clusters [4,62]. This is interpreted as corresponding to collective vibrations of the valence electrons in the directions of the principal axis of a triaxially deformed cluster and has motivated the extension of the jellium model to fully triaxial shapes [66-68]. The triaxial deformations of the uniform background can be classified in terms of the Hill-Wheeler coordinates $\beta$ and $\gamma$ [69]. $\beta$ describes the overall quadrupole deformation. $\gamma = 0^\circ, 120^\circ, 240^\circ$ describe prolate deformations, and $\gamma = 60^\circ, 180^\circ, 300^\circ$ oblate ones; all other values of $\gamma$ give truly triaxial shapes. Let us consider Na$_{12}$ and Na$_{14}$. The potential energy surfaces of those two clusters in the triaxially deformed jellium model have been calculated by Lauritsch et al [66]. In addition to the shape deformation of the positive background, the jellium was also allowed to have a diffuse density profile at the surface [54]. The ground state of Na$_{12}$ is triaxial, with deformation parameters $\beta = 0.54$, $\gamma = 15^\circ$. This structure is energetically well separated from competing prolate and oblate configurations. Na$_{14}$ is characterised by two axially symmetric isomers, prolate and oblate respectively, almost degenerate in energy. The oblate minimum is rather soft in the $\gamma$-direction, whereas the prolate minimum predicts stiffer $\gamma$-vibrations. The pronounced shape isomerism found for both clusters bears some resemblance to that found by fully microscopic quantum chemical [70] and $ab$ initio DFT calculations [71]. The resonance energies of the collective dipole excitations were obtained from the approximate expression

$$\omega_i^2 = \frac{1}{Nm_e} \int n(r) \frac{\partial^2}{\partial r_i^2} V_{ex}(r) d^3r$$

(71)

obtained from the RPA sum rules [6]. In this equation, $V_{ex}$ is the electrostatic potential of the jellium background, $m_e$ is the electronic mass and $i$ runs over the spatial directions, i.e., $r_i = \{x, y, z\}$ for the triaxial clusters and $r_i = \{r, z\}$ for axial ones. The resonance energies, calculated for the ground state of Na$_{12}$ and for the two degenerate minima of Na$_{14}$ are given in Table 4. Three different energies are obtained for Na$_{12}$, reflecting its triaxial shape. The three energies are in qualitative agreement with the experimental peaks [4,62], although the calculated energies are 10-15% too high due to the simple
sum rule approximation used. Each of the two competing axial isomers of Na\textsubscript{14} is characterized by a double peak structure where $\hbar \omega_r$ has double weight compared to $\hbar \omega_z$. The actual strength distribution will be an incoherent superposition of the two isomeric minima.

Kohl et al [72] extended the calculations to a larger set of Na\textsubscript{N} clusters ($N = 2$-20). They have confirmed the results of the spheroidal jellium model: prolate clusters after the magic numbers $N = 2$ and $N = 8$, and oblate ones before $N = 8$ and $N = 20$. However, a transition region formed by triaxial shapes was found separating the prolate and oblate regions. This region is very small between $N = 2$ and $N = 8$, containing only the cluster Na\textsubscript{5}, and is larger in the region between $N = 8$ and $N = 20$. The triaxial minimum is well developed in Na\textsubscript{5} but the others are extremely soft, such that thermal fluctuations will easily wash out the triaxial signatures in the dipole resonance. For cationic Na\textsuperscript{+}_N clusters, Kasperl et al [67] have concluded that the signal of triaxiality on the resonance energies is faint for clusters larger than Na\textsuperscript{+}_6.

The mechanisms responsible for the width of the plasmon resonance have been investigated [73] for spherical clusters (Na\textsuperscript{+}_5, Na\textsuperscript{+}_21, Na\textsuperscript{+}_41) in the framework of the structurally averaged jellium model [74]. In this model the effects of the ionic structure are added in an averaged manner: first, as an additional potential on the electrons, second as an average Madelung energy in the volume, and third as an ionic surface energy. The two leading mechanisms for the line broadening are the fragmentation of the resonance into nearby particle-hole transitions, and splitting through thermal quadrupole fluctuations [52].

12. Approximate account of the ionic structure

The experimental measurements of the photoabsorption cross section of the closed shell cluster Na\textsuperscript{+}_21 show a plasmon resonance in the region 2.65-2.74 eV; more specifically, at 2.65 eV in ref. [61], at 2.68 eV in ref. [62], and at 2.74 eV in ref. [75], with an averaged value of 2.69 eV. This cluster, having 20 electrons, is isoelectronic with Na\textsubscript{20}, but the plasmon resonance occurs at a slightly higher energy in Na\textsuperscript{+}_21, due to the stronger confining potential. A TDLDA calculation for Na\textsuperscript{+}_21 within the
The jellium model, shown in the upper panel of Figure 7 [76], gives the plasmon energy at 2.95 eV, overestimating its energy by 0.2-0.3 eV. Introducing in the calculation nonlocal corrections to exchange and correlation improves the position of the resonance (2.63 eV), but also leads to the appearance of a separated fragmentation peak. This fragmentation of the plasmon peak has not been observed in the experiments, although a shoulder was detected by Borgreen et al [62] and by Reiners et al [75] on the blue side of the peak.

The photoabsorption cross sections obtained with the Spherically Averaged Pseudopotential model (SAPS) are plotted in the bottom panel of the same Figure. The SAPS model [77,78] provides an approximate description of the cluster structure, intermediate between the simple uniform background model and the full treatment of the geometry of the ionic skeleton. Consider a cluster with the ions at positions \( \{R_j\}_{j=1}^N \). If each ion is replaced by a local pseudopotential, \( v_{ps}(|r-R_j|) \), then the total external potential seen by the valence electron cloud is given by

\[
V_{ps}(r) = \sum_{j=1}^{N} v_{ps}(|r-R_j|).
\]

Experience with the spherical jellium model suggest that for clusters with a nearly spherical shape this external potential can be replaced by its spherical average about the cluster center

\[
V_{ps}(r) \rightarrow V^{SAPS}(r).
\]

This simplification greatly reduces the computational effort of calculating the electronic levels since the electrons now move in a spherically symmetric potential well. However the SAPS model goes beyond the Spherical Jellium Model, since: (a) the radial structure of the cluster becomes reflected in the SAPS potential, and (b) the ion-ion interaction is calculated for the true three-dimensional arrangement of the ions [78]. One can set limits of validity to the SAPS model. The cluster cannot be too small, because small clusters substantially deform away from the spherical shape. On the other hand, very large clusters have a tendency to form planar surface facets. The range of intermediate sizes is then the most appropriate one. Returning to \( \text{Na}^{+}_{21} \), the structure of this cluster is rather spherical (\( \text{O}_h \) symmetry in a recent calculation [79]), so the use of the SAPS model is justified. The results are given in the lower panel of Figure 7. The LDA again overestimates the experimental
plasmon energy, but the nonlocal WDA calculation places the plasmon at 2.70 eV; this time the strong fragmentation has disappeared, and only small features remain at 3.0 eV and 3.5 eV, which correlate with the observed shoulders [62,75]. The photoabsorption spectrum of $\text{Na}^+_{14}$ has also been calculated [80] using the SAPS model and the WDA for exchange and correlation. The position and shape of the plasmon resonance is again in good agreement with experiment.

For $\text{Cs}_8$ a fragmentation peak has been observed near the surface plasmon resonance at 1.55 [81,82]. The surface plasmon is obtained at 1.79 eV using the Sherical Jellium Model. The SAPS model predicts a square-antiprism as the ground state geometry of $\text{Cs}_8$ [83]. By adjusting the cluster radius and the core radius of a pseudopotential developed by Manninen [84], the SAPS model leads to a good fit to the experimental plasmon peak and its fragmentation [81,83]. A good fit was not obtained for the geometries tested other than the square antiprism.

In an extension of the SAPS model, Schöne et al [85,86] expand the total ionic pseudopotential of eq. (72) in spherical harmonics about the center of the cluster

$$V_{ps}(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{l=3} \sum_{m=-l}^{l} V_{l,m}(\mathbf{r}) Y_l^m(\theta, \phi). \quad (74)$$

The first term $V_0$ is just the monopole, spherical part of the total ionic potential. This is the SAPS potential. The other part can be included perturbatively up to second order on top of a SAPS calculation. Similar ideas, based on a perturbative introduction of geometrical effects beyond SAPS, were applied by Rubio et al [87] to the fullerene molecule. The perturbative theory can also be developed within the TDLDA formalism, and the method has been applied [85,86] to calculate the optical spectrum of the closed-shell clusters ($\text{Na}_8$, $\text{Na}_9^+$, $\text{Na}_{18}$) and open shell clusters ($\text{Na}_6$, $\text{Na}_{10}$). For the close-shell clusters, the perturbative calculations predict a photoabsorption spectrum in agreement with that of the SAPS model and justify the validity of this model for magic clusters. For small open-shell clusters there are differences, as expected. The geometry of $\text{Na}_6$ is a planar-like pentagonal pyramid ($C_{5v}$ symmetry) [71]. The SAPS spectrum [85] gives a main absorption line at 2.3 eV. In contrast, the perturbative calculation for the $C_{5v}$ geometry gives several peaks in the energy range 2.0-2.8 eV, in qualitative agreement with the experimental results of Wang et al [88], and also with ab
initio quantum chemical calculations [89]. Surprisingly, the spectrum of Na$_{10}$, given in Figure 8, does not resemble that of the spheroidal jellium model [64,65], and this appears to indicate a pronounced effect of the pseudopotentials beyond the jellium approximation. In summary, quantitative agreement with experiment was obtained by the perturbative method, but this method becomes difficult for clusters with low symmetry.

13. Mixed metal clusters

Experiments with metal vapors [90,91] have shown that some changes occur in the magic numbers of alkali metal clusters when these are doped with divalent impurities: Ba, Sr, Eu, Ca, Yb, Mg and Zn dopants in Na clusters, and Mg, Hg and Zn dopants in K clusters. These authors concentrated on the case of clusters containing a single dopant atom. For some impurities a new magic cluster corresponding to ten valence electrons is found, for instance Na$_8$Mg, K$_8$Mg, K$_8$Hg, Na$_8$Zn and K$_8$Zn, and at the same time the magic number corresponding to eighteen valence electrons vanished. The single coordinate $\Delta n_e = n_{0,e}(\text{impurity}) - n_{0,e}(\text{host})$, that is, the difference between the average conduction electron densities in the pure host and impurity metals, allows to separate the doped clusters into two subsets [92]. Values of $\Delta n_e$ roughly higher than 0.008 e/a.u.$^3$ induce changes in the magic numbers. In contrast there are no changes for $\Delta n_e < 0.008$ e/a.u.$^3$. The success of this coordinate suggests a simple extension of the Spherical Jellium model [92]. The impurity is embedded in a host cluster with a background density equal to $n_{0,e}(\text{host})$. The impurity, placed at the center of the host cluster, is then characterised by a positive background with density $n_{0,e}(\text{impurity})$ and radius $R_{\text{imp}}$. The radius of the doped cluster is determined by $R_{\text{imp}}$ and the number of host atoms. Calculations for this jellium-on-jellium model show that the binding energy of the electrons with $s$-character ($l = 0$) increases in comparison to the undoped cluster because the presence of the divalent impurity induces a more attractive effective potential in the central region of the cluster, whereas the binding energies of electrons with $l \geq 1$ change very little. The main effect on the electronic structure is that the magnitude of the gap between the $2s$ and $1d$ shells decreases with increasing $\Delta n_e$. When $\Delta n_e$ becomes roughly 0.008 e/a.u.$^3$, a reordering of these two subshells occurs.
and the filling order changes from the original 1s 1p 1d 2s to the new one 1s 1p 2s 1d. Clusters with 10 valence electrons then have a closed-shell configuration 1s^2 1p^6 2s^2, which accounts for the experimental observation of the new magic number. The magic number corresponding to 20 electrons, corresponding to the electronic configuration 1s^2 1p^6 2s^2 1d^10, is still present, but evidently there is no shell-closing for 18 electrons.

The optical response of doped clusters has been studied by Yannouleas et al using the jellium-on-jellium model [93]. The calculated spectrum of Na_8Zn is characterized by two closely spaced lines at 2.87 eV, carrying 26 % of the total strength, and a stronger line at 2.57 eV which carries 42 % of the strength. This is in good agreement with the experimental double peak, formed by a higher energy component at 2.97 eV, which carries a smaller amount of strength than the lower energy component at 2.63 eV. The fragmentation of the plasmon peak is due to its degeneracy with the 2s → 2p and 1p → 3s particle-hole transitions. This result was obtained for an electron density parameter r_s(Zn) = 1.15 a.u. (see equation (20)), a value substantially smaller than the typical value of r_s = 2.31 a.u. for bulk Zn. The smaller value of r_s(Zn) produces a strong attractive potential at the impurity site, which leads to the downwards shift of those transitions required for the degeneracy with the plasmon to develop. The spectrum of pure Na_8 contains a single line at 2.53 eV, so the effect of the Zn impurity is evident. The need for such a small value of r_s may be related to the application of the jellium model to an element, like Zn, at the end of the transition metal group. Balbás et al. [94] have calculated the optical response of Na_8Zn using the SAPS model, with the Zn atom at the center of the cluster. Two peaks are obtained at 2.68 eV and 2.9 eV. The second one was interpreted as a fragmentation of the surface plasmon induced by its proximity to the ionization threshold, an interpretation that differs from that proposed by Yannouleas et al [93].

As another example of the influence of impurities on the optical response Yannouleas et al considered the group formed by K_{19}Rb, K_{20} and K_{19}Na, all of them with 20 valence electrons. The calculated optical spectrum of K_{20} shown in Figure 9, exhibits a split plasmon due to a degeneracy between the collective plasmon and a 2s → 3p particle-hole transition. In the case of K_{19}Na, the Na impurity, with a smaller r_s than the host, shifts the 2s level downwards, so the energy of the 2s →
3p transition increases. At the same time the energy of the plasmon remains unchanged, and the consequence is that a single line dominates the spectrum. The opposite effect occurs for a Rb impurity. The energy of the \(2s \rightarrow 3p\) transition is lowered and the plasmon splitting is more pronounced.

The absorption spectrum of Cs\(_{10}\)O shows two peaks at 1.39 eV and 1.54 eV \[81,82\]. One can expect the 2\(p\) shell of the Oxygen atom to be filled by two electrons provided by the Cs atoms. In this way, Yannouleas and Broglia \[95\] have treated Cs\(_{10}\)O as a system with eight active electrons. These authors employed a modified jellium potential in which the central part of the cluster was made less attractive, in order to simulate the repulsive effect of the oxygen anion O\(^2^-\). The fragmentation of the plasmon was reproduced, although a difference of \(\approx 0.2\) eV remained between the positions of the theoretical and experimental peaks. Calculations using the SAPS model show that the absorption spectrum is sensitive to the radius of the cluster \[83\], and this can be adjusted to obtain a good description of the spectrum. Also, inclusion of the \(p\)-electrons of the oxygen atom is required, since particle-hole transitions from the \(p\) shell to the unoccupied 4\(s\) shell contribute to the fragmentation of the collective resonance. The cluster geometry used in the calculations was the one predicted by the SAPS model, with the Oxygen atom at the center of a square pyramid with each of the five faces capped by one Cs atom.

A common phenomenon in binary metallic alloys is the preferential segregation of one of the components at the surface \[96,97\]. Surface segregation affects also the collective electronic response of clusters. The ground state structure of Na\(_{20}\)K\(_{20}\) obtained with the SAPS model is composed of three layers surrounding a central Na atom. All the Potassium atoms are on the surface and the two inner layers have eleven and eight Na atoms respectively. The calculated photoabsorption spectrum \[98\] shows a collective resonance peak at 2.1 eV. The tail of the resonance extends up to 3 eV and concentrates a sizable amount of oscillator strength. The position of the collective resonance is closer to the corresponding resonance of pure K clusters, calculated with the same method, compared to pure Na clusters, and this is a manifestation of the fact that the cluster surface, whose electron density contributes most to the collective excitation, is formed by K atoms. A calculation of the
photoabsorption spectrum for other isomers allows to analyze the sensitivity of the spectrum to the structural features. When the positions of some Na and K atoms are simply exchanged, preserving other features of the cluster geometry, a shift of the resonance peak to higher energies occurs as Na replaces K on the surface. More drastic variations of the structure produce pronounced changes in the spectrum, like the broadening and fragmentation of the plasmon peak. The optical response of mixed Li-Na clusters has also been studied [94]. In summary, the shape of the photoabsorption spectrum is sensitive to the cluster geometry and to the degree of segregation of one component to the surface; so, a comparison between measured and calculated spectra may be useful to elucidate segregation effects in mixed clusters.

14. Simple model for the photoabsorption spectrum of Fullerenes

Extensions of the jellium model have been applied to more complex systems, like carbon fullerenes [87]. Experimental studies [99-103] have shown the presence of two collective excitations in C\(_{60}\), a broad one in the region 15-25 eV, associated with the \(\sigma\) electrons of the cage, and the other around 6 eV, that was interpreted as a collective oscillation of the \(\pi\)-electrons. The electrons in \(\sigma\) orbitals (three electrons per C atom) link neighbouring atoms in the cage and provide most of the cohesion. On the other hand, the \(\pi\) orbitals extend in and out of the cage and are more delocalized. For this reason, to describe the response of the \(\pi\) electrons, a model [87] has been used that simulates the C\(_{60}\) cage by a thin spherical shell of positive charge

\[
n_+(r) = \begin{cases} n_1, & R - \Delta_1 \leq r \leq R + \Delta_1 \\ 0, & \text{otherwise} \end{cases}
\]

with the observed radius \(R = 6.64\) a.u [104] and a width \(2\Delta_1\) in the range 0.8-1.0 a.u., compensated by a distribution of \(\pi\) electrons (one \(\pi\) electron per C atom) selfconsistently calculated. The constant \(n_1\) is easily related to \(R, \Delta_1\) and the total number of \(\pi\) electrons (60). The calculated plasmon resonances of \(C_{60}\) and \(C_{60}^+\) are roughly in the right position [87,105]

The model was extended to \(C_{60}\) coated by a layer of Na atoms [105]. In that case, the positive background was modeled as two concentric spherical thin layers, one on top of the other, the inner
one, of thickness $2\Delta_1$, representing the fullerene cage, and the outer one, of thickness $\Delta_2$, representing the alkali coating; that is,

$$
n_n(r) = \begin{cases} 
n_1, & R - \Delta_1 \leq r \leq R + \Delta_1 \\
n_2, & R + \Delta_1 \leq r \leq R + \Delta_1 + \Delta_2 \\
0, & \text{otherwise} \end{cases}
$$

(76)

The background density $n_2$ of the external layer was fixed equal to its value for bulk Na metal, $n_2 = 0.004$ e/a.u.$^3$, and the thickness $\Delta_2$ then depends on the number of coating Na atoms. The background density and the selfconsistent electron density of $[C_{60}Na_{93}]^+$ are plotted in Fig.10. The electron density shows two different decay lengths. This cluster has an outer surface which resembles a lot the surface of pure Na clusters. The development of the coating metallic layer becomes reflected in the calculated photoabsorption spectrum, shown in Figure 11.

For small Na coverage, like in $[C_{60}Na_{13}]^+$, the interaction between the electrons originating from the Na atoms and the unoccupied levels of $C_{60}$ is strong and the TDLDA calculation predicts a spreading of the $\pi$-plasmon of $C_{60}$ down to lower energies by more than 1eV, and a reduction of its amplitude. This is mainly due to the fragmentation of the collective resonance caused by the interaction with particle-hole transitions. Then the characteristic features of the $C_{60}$ plasmon progressively vanish as the number of coating Na atoms grows. At the same time, a new feature develops at lower energies that can be related to the surface plasmon of pure Na clusters. For $[C_{60}Na_{93}]^+$ the Na surface plasmon is well developed, and the cluster responds much like a pure ionized Na cluster; the resonance has, nevertheless, a broad tail at high energies.

The fragmentation of the peak may have relevance for the interpretation of experiments by Martin and coworkers [106]. These authors have produced $C_{60}$ clusters coated with Cs. For large coverage, say $[C_{60}Cs_N]^+$ with $N \approx 300$, the photoabsorption spectrum is very similar to that of large pure $Cs_N$ clusters, except for a more intense tail. As $N$ decreases a fragmentation of the plasmon occurs that resembles that obtained in the TDLDA calculations for $[C_{60}Na_N]^+$. Thus, the TDLDA based on the model of two spherical jellium slabs appears to afford a plausible explanation for the optical absorption spectrum of alkali-coated $C_{60}$ clusters.
15. Full account of the cluster structure

TDLDA calculations of the optical spectrum with a full account of the geometry of the cluster have also been performed. Apart from being more realistic compared to the other calculations discussed above, which retain only the overall shape characteristics, these new calculations can provide a useful method to determine the cluster geometries. Sometimes, the differences in binding energy between the ground state and some low lying isomers obtained by ab initio calculations are so small as to cast doubts about the calculated lowest energy structure, and a comparison of the experimental optical spectrum and those calculated for several isomers with similar energies can help in the identification of the ground state.

A method based on a space and time representation of the response functions of extended systems has been developed that takes advantage of the rather sparse Hamiltonian matrix in a coordinate representation [107,108]. The advantage is related to the localization range of the independent-particle susceptibility $\chi_s(r,r';\omega)$ and other response functions, since localized objects are easily described in real space. In practice, the response functions of non-metallic systems decay rapidly as $|r-r'| \to \infty$, so that for each $r$, $\chi_s(r,r';\omega)$ needs to be calculated only for $r'$ inside a region of a certain radius $R_{max}$ around $r$. This is the origin of the success of recent N-linear methods (where N is the number of atoms in the unit cell) proposed to perform band-structure calculations for solids [109-113]. However, for metals and small gap semiconductors the decay rate may be slow and $R_{max}$ may span many unit cells. This problem can be solved by a mixed-space representation $\chi_q(r,r';\omega)$ of the response functions, where $r$ and $r'$ are restricted to a single cell and $q$ spans the irreducible part of the Brillouin zone [108]. The method, described in references [26] and [108], has been adapted to clusters by using a supercell formalism, in which the unit cell containing the cluster is periodically repeated in space, and this allows to expand the wave functions in a basis of plane waves. The volume of the cell containing the cluster has to be sufficiently large to avoid the interaction between clusters in neighbor cells; that is, a high part of the volume of the cell is empty.
The photoabsorption cross section of Na$_8$, calculated by this method [114], is in excellent agreement with experiment, with the calculated position of the plasmon peak at 2.55 eV and the experimental one at 2.53 eV [4, 51]. The TDLDA photoabsorption cross section of Li$_8$ is given by the continuous curve in Figure 12. The calculated ground state structure, given in the inset, is a centered trigonal prism with an atom capping one of the lateral faces. The averaged value of the static dipole polarizability $(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$ is $97\ A^3$, which is larger than the value of $63\ A^3$ obtained in the spherical jellium model [114]. From classical arguments, a larger polarizability corresponds to a lower resonance frequency, so a redshift of the resonance with respect to the jellium value of 3.5 eV should be expected. Indeed, the effect of explicitly accounting for the cluster structure produces a redshift of 1 eV which leads to very good agreement between the calculated resonance at 2.45 eV and the experimental value of 2.5 eV [115] (compare the position of the peak of the continuous curve with that of the arrow in Figure 12). The nearly isotropic polarizability tensor explains the presence of a single resonance. The red shift can be tracked down to an increase of the electron effective mass, an effect of the Li ionic pseudopotential.

The computed structures of silicon clusters [114], given in the insets in Figure 13, agree with other calculations [116,117] and with Raman experiments [118]. A planar rhombus (D$_{2h}$ symmetry) is obtained for Si$_4$ and two nearly isoenergetic structures for Si$_6$: a distorted octahedron (D$_{4h}$) and an edge-capped trigonal bypyramid (C$_{2v}$), the octahedron being slightly more stable by $\approx 0.02$ eV. Could structural isomers be distinguished from their absorption spectra? This question is analyzed in Figure 13, where the calculated single photon averaged absorption profiles have been plotted for two different isomers of each of these two clusters, Si$_4$ and Si$_6$ (the second isomer of Si$_4$ is the tetrahedron). All the spectra have been broadened by 0.1 eV to simulate finite temperature effects [52]. The calculated spectra of different isomers are sufficiently different, and the conclusion is that the optical spectrum contains structural information, so the comparison between calculated and measured optical spectra can provide a powerful tool to assign structures to the clusters. Even more striking differences in the spectra are obtained if each of the tensor components of the absorption cross section are considered separately instead of the averaged one. Exchange-correlation effects play
here a minor role as compared to the metallic clusters (the same observation is known to hold for the bulk). Surface and confinement effects are responsible for the appearance of absorption in the optical range seen in the TDLDA spectra for the two Silicon clusters. In fact, this effect could be related to the luminescence of porous Silicon [119], showing that small clusters could present different and very interesting optical properties as compared to their bulk counterpart.

Other authors have been accounted for the cluster structure in the TDLDA, using different methods. Vasiliev et al [39] have calculated the optical spectrum of small Sodium clusters (Na$_2$, Na$_4$, and Na$_8$), using the coupling matrix method (see Section 6). The results obtained from the exact calculation, equation (59), and the two approximate expressions (60) and (61), are reproduced in Figure 14. The approximate expressions do not give a good account of the experimental data. On the other hand the exact TDLDA calculation reproduces remarkably the experimental spectral shape [51,120-122], and the peak positions agree with experiment within 0.1-0.2 eV. The calculated spectrum of Na$_2$ exhibits three peaks in the 2-5 eV range. Na$_4$ has a rhombic shape and its spectrum consists of three peaks in the 1.5-3.0 eV range, and a broader feature at higher energy. The results are almost as accurate as the spectra calculated by the Configuration Interaction method [123]. For increasing cluster size the spacing between the discrete line decreases, evolving towards the collective plasmon. For Na$_8$, with the rather spherical structure of a bicapped octahedron, a single peak is already obtained. The importance of electronic screening is evident by comparing the different panels in the Figure.

Pacheco and Martins [124] have studied the sensitivity of the calculated photoabsorption cross sections of the magic clusters Li$_8$, Li$_{20}$, Na$_8$ and Na$_{20}$ to the use of different ab initio nonlocal pseudopotentials. The pseudopotential of Bachelet, Hamman and Schlüter (BHS) [125] and the pseudopotential of Troulliers and Martins (TM) [126] were employed, together with the LDA for exchange and correlation. The different pseudopotentials lead to the same equilibrium geometries obtained previously for Li and Na clusters in the LDA: a bicapped octahedron for Na$_8$ [127] and a trigonal prism for Li$_8$ [114,128]; the structures obtained for the 20-atom clusters are more difficult to classify. However the average bond lengths depend on the input pseudopotential, and the bond lengths calculated with the BHS pseudopotential are smaller than those obtained with the TM
pseudopotential. The difference is sizable for sodium clusters but minor in the Lithium case. As a consequence of the different average bond lengths, differences are also found in the calculated static polarizabilities. The multipeaked line shapes of the photoabsorption cross sections are nearly identical, except for small overall energy shifts. Compared to the jellium LDA spectrum of Figure 4, the spectrum of Na$_{20}$ obtained by taking into account the full geometry of the ionic background is slightly shifted to lower energies, that is, in the correct direction.

Very small mixed clusters have been studied by quantum chemical ab initio methods. Motivated by the measurements of the optical absorption spectra of LiNa$_3$ and Li$_2$Na$_2$ [129], Configuration Interaction (CI) calculations have been performed for those two clusters [130], as well as Hartree-Fock calculations for the whole family Li$_m$Na$_{4-m}$ [131]. The optical response was obtained in both cases from CI calculations for excited electronic states. The two theoretical studies predict planar rhombic forms as the most stable structures: slightly distorted for LiNa$_3$ and Li$_2$Na , and undistorted for Li$_4$, Na$_4$ and Li$_2$Na$_2$ . The photoabsorption spectrum is sensitive to $m$, that is, to the relative proportion of Li and Na. The spectrum of Na$_4$ resembles that obtained from the Mie-Drude theory for an ellipsoidal droplet with three different axes. But, as Li atoms replace Na atoms, the deviations from the Mie theory increase. The measured spectra of LiNa$_3$ and Li$_2$Na$_2$ are explained by the ab initio calculations. The calculations found low lying isomers in each Li$_m$Na$_{4-m}$ case, corresponding to different ways of arranging the Li and Na atoms in the four vertices of the rhombus. The comparison between the experimental absorption spectrum of Li$_2$Na$_2$ and the spectra calculated for the three isomers detected, confirmed that the best agreement is obtained for the lowest energy isomer. On the other hand, the calculated spectra for the two singlet isomers of LiNa$_3$ are so similar that it was not possible to distinguish which isomer or whether a combination of both singlet isomers contributes to the measured spectrum.

TDLDA calculations for the whole Na$_{8,m}$Li$_m$ family [132] obtained single (plasmon) peaks at both ends of the series, Li$_8$ and Na$_8$, consistent with a spherically symmetric electron density for both clusters. The replacement of one or two atoms in the homogeneous clusters produces an spheroidal deformation of the density and introduces extra shoulders in the spectrum. In the middle of the series, for Li$_3$Na$_3$ and Li$_4$Na$_4$, the resonance is fragmented in two close peaks. These two clusters have
tetrahedral symmetry and, as a rule, the oscillator strength in the absorption spectrum of clusters with nonspherical shape is spread over a wide energy range, thus leading to a broader spectra.

16. Optical response of fissioning clusters

Multiply charged metal clusters, like $\text{Na}_{q^+}^N$ are less stable than the corresponding neutrals $\text{Na}_N$ due to the coulombic repulsion of the unbalanced positive charges, and can easily experience a process of fission. The process of cluster fission has close analogies to the fission of nuclei [133]. In both cases a charged droplet will become unstable towards the division into two or more fragments. In simple terms, the multiply charged cluster can be viewed as a droplet, which due to the unbalanced excess positive charge tends to deform through elongated shapes keeping the total volume constant. But the shape deformation increases the surface area and then the surface energy of the cluster. This decreases the cohesion of the cluster and builds up an energy barrier that prevents the spontaneous fission for large cluster sizes, even when the sum of the energies of the fission products is lower than the energy of the multiply charged parent. For small clusters, on the other hand, the coulombic repulsion may be so strong that there is no barrier, and fission occurs spontaneously. Optical spectroscopy has been proposed as a tool to follow the dynamics of fragmentation along the fission path [134]. As an example let us consider the symmetric fission of $\text{Na}_{18}^{2+}$, that is,

$$\text{Na}_{18}^{2+} \rightarrow \text{Na}_9^+ + \text{Na}_9^+.$$ (77)

The results of TDLDA calculations of the optical spectrum [134] along the fission path are given in Figure 15. The Cylindrically Average Pseudopotential (CAPS) model was employed to calculate the ionic and electronic distributions. The CAPS model can be viewed as an extension of the SAPS model considered in Section 12. The CAPS model is based on the observation that most clusters of simple metals have axial symmetry. Taking up this idea Montag and Reinhard [135] have proposed to replace the total external ionic pseudopotential by its cylindrical average. Using cylindrical coordinates, the CAPS potential then becomes
\[ V^{\text{CAPS}}(z, \rho) = \sum_{j=1}^{N} \tilde{V}_{ps}(z; \rho ; z_j, \rho_j), \]  

(78)

\[ \tilde{V}_{ps}(z; \rho ; z_j, \rho_j) = \frac{1}{2 \pi} \int_{0}^{2\pi} \tilde{V}_{ps}(|\mathbf{r} - \mathbf{R}_j|) d\phi. \]  

(79)

A proper choice of the \( z \) axis is critical for the success of the method. Montag and Reinhard considered the inertia tensor \( \hat{I} \) of the ionic distribution, and identified the \( z \) axis with the principal axis of \( \hat{I} \) whose momentum \( I_i \) deviates most from the average momentum \( \bar{I} = (I_1 + I_2 + I_3)/3 \). Since the electrons see an axially symmetric potential, their wave functions separate accordingly as

\[ \phi_{eq}(\rho, \varphi, z) = R_{eq}(\rho, z) e^{-\varphi}. \]  

(80)

The calculation of the ground state geometry and the electronic structure then proceeds by an interlaced iteration of the Kohn-Sham equations and the ionic stationary conditions.

The energy of the ground state of \( \text{Na}_{18}^{2+} \) corresponds to the point labelled A in the energy curve of Figure 15. Its ionic configuration (not shown in the Figure) hints at preformed subunits \( \text{Na}_{15}^{+} \) and \( \text{Na}_{3}^{+} \), which reflects the high stability of the magic two-electron cluster \( \text{Na}_{3}^{+} \) [136]. Nevertheless, the barriers for the asymmetric and symmetric fission channels are practically equal [136,137]. Several cluster configurations along the symmetric fission channel are shown on the upper right side of Figure 15, together with the corresponding electronic distributions. To calculate those configurations, the ions of the cluster are divided in two groups, each one with 9 ions (to simulate the symmetric fragmentation), and a constraint is set up on the distance \( d \) between the centers of mass of these two fragments. The electronic distribution and the ionic configuration are then optimized for each value of \( d \) in an increasing series of fixed distances \( d \). A marked structural change occurs between configurations A and B (where symmetry is established). This rearrangement corresponds to a large difference in energy between the two configurations. Ionic scission takes place at stage D only shortly before the saddle configuration E, while the electron cloud breaks up rather late after the saddle point, around configuration F.

The linear optical response, shown on the left side of Figure 15, gives an enlightening picture of the various stages along the fission path. The ground state configuration A exhibits a pronounced
resonance between 2 and 2.2 eV. With increasing cluster deformation along the fission path we first observe (basically up to stage D) a gradual increase in the fragmentation of the spectrum, but still centered around 2 eV. The connectivity of the electron cloud still existing in stages C and D has the effect to center the dipole spectrum around 2 eV, while the ions are already fully separated at stage D.

A marked change occurs when the electron densities separate at stage F and beyond. The fragmentation of the spectrum disappears and is replaced by the clean plasmon resonance of free Na$_9^+$ around 2.7-2.8 eV. The optical response thus provides a tool of analysis of the various configurations along the fission path. It might be experimentally feasible to follow such a fission path by femtosecond time-resolved recording of the electronic response following short laser pulses, as done nowadays for mapping the isomerization paths of biological photoreceptors and chemical reaction path of molecules [138,139]. One might even hope to have access to fission time scales and thus be able to estimate viscosity effects, in a way somewhat similar to the nuclear case.

17. Thermal line broadening

In order to compare with experiment, most TDDFT calculations perform an ad hoc broadening of the photoabsorption spectrum: the spectral lines, calculated for a static geometrical configuration of the cluster, are broadened through convolution with Gaussian or Lorentzian functions [50,65,114]. But a first principles description of absolute magnitudes, peak positions and line broadening can be achieved by calculating the photoabsorption cross sections along finite temperature Molecular Dynamics simulation trajectories. Shape fluctuations were introduced to account for the line broadening of simple metal clusters [52], with good results for Na clusters. A step forward was taken by Pacheco and Schöne [140], by treating in perturbation theory the deviation of the ionic potential from being spherical. The Montecarlo simulations performed in this work mimic the effect of temperature on the linewidth and the position of the resonance peaks. However, true first principles calculations have only been done recently by Moseler et al [141]. They have calculated the TDLDA optical spectra of Na$_3^+$, Na$_5^+$ and Na$_9^+$ at finite temperatures. The excitation energies were calculated by solving the eigenvalue problem [38] of equation (59) and averaging the calculated cross
sections for a time propagation of 10 ps. The results are shown in Figure 16. The structure of Na$_3^+$ is an equilateral triangle. Its calculated spectrum of at T = 100 K, given by the histograms in panel (a) of the Figure, shows two peaks. The low energy peak originates from two transitions ($h\omega_1 = h\omega_2 = 2.65\text{eV}$) from the occupied $s$-like state to two empty $p$-like states with orbitals in the plane of the cluster. The three relevant orbitals are shown in the inset on the left of panel (a), where they are labelled as 1, 2 and 3 respectively. The other peak, centered at an energy of 3.41 eV, is due to the excitation to the other $p$-like orbital, perpendicular to the cluster plane (see the inset on the right side of the same panel). The positions of the two calculated peaks agree well with the experimental spectrum, given by the continuous line [142]. The intensity and width of the low energy peak are correctly predicted, but the measured high energy peak is less intense than the calculated one. The reason is that the experimental cross section $\sigma(\omega)$ is determined by measuring the photodepletion of the Na$_3^+$ intensity due to dissociation following the absorption of one photon. The two $p$-like states in the cluster plane are antibonding, so excitation into these states promotes dissociation, but excitation into the $p$-like state perpendicular to the cluster plane does not have a direct destabilizing effect. Thermal motion distorts the symmetry of Na$_3^+$ and lifts the degeneracy of the $\omega_1$ and $\omega_2$ transitions. In addition, the mean bond distance in the cluster is anticorrelated with the average of $\omega_1$ and $\omega_2$, and also with $\omega_3$. Consequently, the linewidth can be explained by the combined effect of (1) the line splitting caused by symmetry breaking (called degeneracy lifting by Moseler et al, and (2) breathing vibrations (or spectral sweeping mechanism).

At a temperature of 100 K the dynamics of Na$_3^+$ distorts the ground state $D_{2d}$ symmetry (compare structures $\alpha$ and $\beta$ in the inset in panel (b), where the left triangle of structure $\beta$ is more elongated compared to structure $\alpha$) and fragments the absorption line at $h\omega = 2.8\text{eV}$ into two spectral lines (compare the oscillator strengths given in the upper-right inset in panel (b)). The increase of T to 300 K results in bent geometries (structure $\gamma$ in panel (c)). In this case the low energy line at $\approx 2\text{eV}$ is fragmented. All the lines are further broadened by the effect of the breathing modes. For larger clusters, thermal isomerization leads to another line-broadening mechanism, which adds to the other
two discussed above. The ground state of Na$_9^+$ is oblate (the contours of constant electron density have the shape of an ideal oblate spheroid). Consequently the absorption lines are distributed in a bimodal manner, with further broadening arising from the line fragmentation and breading mechanisms. By increasing the temperature to 450 K, the spectrum transforms to one with a single broad maximum. The main reason for the change in shape is the transformation between the low temperature ground state structure $\alpha$ (a tricapped trigonal prism) and the isomer labelled $\beta$. The static spectrum of this isomer is shifted to lower energies compared to that of the ground state, and the broad spectrum at 450 K is due to contributions from both isomers.

18. Full solution of the time dependent Kohn-Sham equations

18.1 Theory

Another efficient method exists to calculate the optical spectrum in finite systems, based on directly solving the time-dependent Kohn-Sham equations of DFT in response to the external laser field. This method, originally used for the study of nuclear reactions [143] has been later applied to clusters [144-147]. The set of equations to be solved for the combined electron and ion dynamics is formed by the time dependent KS equations (30)-(31), together with the Newton equations for the motion of the ions

$$m_\alpha \frac{d^2 R_\alpha}{dt^2} = F_\alpha(R_\alpha, t).$$

(81)

The applied perturbing field $V_{\text{ext}}(\mathbf{r}, t)$ appearing in equation (30) is, in this case, the laser potential $V_{\text{laser}}(\mathbf{r}, t)$ describing the classical time-dependent external electromagnetic field acting on the system. In the Newton’s equations for the ions, $R_\alpha$ stands for the position of the ion labelled $\alpha$, $m_\alpha$ for its mass, and $F_\alpha$ is the instantaneous force on that ion. This force is calculated through the Ehrenfest theorem

$$F_\alpha(R_\alpha, t) = -\left\langle \Psi(t) \left| \frac{\partial}{\partial R_\alpha} \hat{H} \right| \Psi(t) \right\rangle.$$

(82)
This is just the extension of the Hellmann-Feynman theorem to the time-dependent domain. There are no Pulay corrections to this expression when the Kohn-Sham wave functions are expanded in a regular grid space, but this would not be the case if one uses localized basis sets [146,148,149].

The ground state of the electronic system in the nuclear equilibrium configuration, i.e., the solution of the ground state Kohn-Sham equations

\[
\left[ -\frac{1}{2} \nabla^2 + V_{\mu} (\mathbf{r}) + V_{xc} (\mathbf{r}) + V_N (\mathbf{r}) \right] \psi_i (\mathbf{r}) = \varepsilon_i \psi_i (\mathbf{r}) ,
\]

is the starting point for the time-dependent simulations. The Kohn-Sham orbitals are then propagated in time as

\[
\psi_i (\mathbf{r}, t + \Delta t) = e^{-i\mathcal{H}_0 \Delta t} \psi_i (\mathbf{r}, t).
\]

In this method, only occupied states need to be propagated and there is no need of computing empty states.

To obtain the linear optical absorption spectrum one can follow an scheme proposed by Yabana and Bertsch [144,147], and excite all frequencies of the system by giving a small momentum \( \mathbf{k} \) to the electrons. This is achieved by initially transforming the wave functions according to

\[
\psi_i (\mathbf{r}, \delta t) = e^{i\mathbf{k} \cdot \mathbf{r}} \psi_i (\mathbf{r}, 0) ,
\]

and then propagating these wave functions for some (finite) time. The spectrum can then be obtained from the expression of the dipole strength function \( S(\omega) \)

\[
S(\omega) = \frac{2\omega}{\pi} \text{Im} \alpha(\omega)
\]

where the dynamical polarizability \( \alpha(\omega) \) is essentially the Fourier transform of the dipole moment of the system

\[
\alpha(\omega) = \frac{1}{k} \int e^{i\omega t} [D(t) - D(0)] dt .
\]
With this definition, the Thomas-Reiche-Kuhn \( f \)-sum rule for the number of electrons, \( N \), is given by the integral

\[
N = \int S(\omega) d\omega. \tag{89}
\]

This sum rule can be used to check the quality of the calculations. Another check is energy conservation, which the TDDFT respects when there is no external field applied.

For the purposes of obtaining nonlinear optical properties, the evolution of the system under the influence of a laser field, treated in the dipole approximation (although this constraint can be removed), is followed. The emitted harmonic spectrum can then be calculated from the acceleration of the dipole moment \([150,151]\)

\[
H(\omega) \propto \left| \int dt \, e^{i\omega t} \frac{d^2}{dt^2} D(t) \right|^2. \tag{90}
\]

In the implementation of Rubio and coworkers, who have developed a code called OCTOPUS \([146]\), charge is absorbed at the boundaries of the simulation region during the propagation. This can be simulated by using an imaginary absorbing potential \([152]\) which is added to the Kohn-Sham potential, that is,

\[
V_{\text{eff}}(r,t) = V_{\text{KS}}(r,t) - iV_{\text{abs}}(r), \tag{91}
\]

where \( V_{\text{abs}}(r) \) is zero in the inner region of the simulation box and rises smoothly till the edges. By adjusting both the height and the shape of the potential one can select which momenta are absorbed, and prevent the unwanted reflections at the boundary. Another option for simulating the absorption is to use a mask. In this case the wave function is multiplied at each time step by a function which is 1 in the inner region of the simulation box and gradually goes to zero at the borders. The absorbed charged can be interpreted as the ionization probability and can be used to estimate the photo-electron spectra. The box size has to be big enough so that the physical system is not perturbed by the absorbing boundaries.

18.2 Applications to carbon clusters
Medium size carbon clusters are predicted to have a wide variety of isomers with the form of cages, bowls, planar graphitic structures, rings and linear chains. The theoretical and experimental study of the different isomers may help to understand the way fullerenes form [153]. The smallest possible fullerene, consisting of 12 pentagons with no graphitic hexagons intercalated, is an isomer of $C_{20}$. Other low energy isomers of $C_{20}$ include a bowl (which can be considered as a fragment of $C_{60}$), several rings and other closed 3-dimensional arrangements. Prinzbach et al [154] have reported the production of the cage and bowl members of the family. The smallest fullerene cannot be expected to form spontaneously, but has been produced from the precursor $C_{20}H_{20}$. The bowl was produced in the same way, and photoelectron spectroscopy has been used to distinguish between the different species.

It is very difficult to make reliable theoretical predictions of the most stable structure of $C_{20}$. In fact, different levels of theory favor different isomers. At the Hartree-Fock level, the ring is the ground state, followed by the bowl and the cage [155]. Density functional theory in the LDA approximation reverses the order, predicting the cage as the lowest energy structure [156,157]. The use of better functionals based on the generalized gradient approximation (GGA) does not clarify matters: the ordering of the isomers depends on the correction used [155-157]. Quantum Monte Carlo (QMC) and coupled cluster (CC) methods have also been applied in an attempt to resolve the issue, yielding bowl-ring-cage ordering using the former method [155] and cage-bowl-ring using the latter [158]. Furthermore, it seems that the results are sensitive to the pseudopotential [158]. Changing slightly the pseudopotential cutoff radius may actually reverse the ordering of the isomers. Another complication is that entropy effects affect the relative stability, and the calculated free energies as a function of the temperature [159] have been used to assign the dominant species generated in experiments by vaporizing graphite or prepared from precursors. Thus it is important to find experimental methods to determine the structure that are sensitive enough to be usable with the available cluster beam intensities, and optical spectroscopy fulfills the requirements. The geometrical structures of six members of the $C_{20}$ family are given in Figure 17: the smallest fullerene (cage), which is a Jahn-Teller distorted dodecahedron, the ring, the bowl, and three cage-like structures,
labelled as (d), (e) and (f). Structures (d) and (f), related by a Stone-Wales transformation\cite{160}, are composed of four hexagons, four pentagons, and four four-membered rings. These structures are the six isomers with lower energy as calculated by Jones within the LDA approximation \cite{161}. Other structures, such as bicyclic rings, chains and tadpoles may be favoured by entropy at high temperature and have been observed experimentally. However, neither of them seem to be a possible low temperature ground state. The results of TDDFT calculations of the optical absorption are shown in the same Figure \cite{162}. Table 5 gives the energies and strengths of the lowest transitions with appreciable strength. These results were obtained by solving the time-dependent KS equations, with the LDA for exchange and correlation, and representing the wave functions on a uniform spatial grid. The norm-conserving soft-core pseudopotentials of Troullier and Martins \cite{126} were used to avoid explicit consideration of the 1s core electrons.

The dipole strength functions shown have been averaged over all orientations of the system. In the case of the ring, the response in the direction perpendicular to the ring plane is almost negligible below 8 eV compared with the response within the plane. Also for the quasi-planar bowl isomer the perpendicular response is extremely weak in that energy range. While present molecular beam experiments are not able to discriminate between the different spatial directions, the averaged spectra are still sufficiently different to discriminate between the different structures without ambiguity. Two regions can be distinguished in all the graphs: (a) the peaks which can be seen in the near ultraviolet, and (b) a broad absorption that starts at around 7.5 eV. Focussing attention on the lower energy peaks, the ring exhibits the largest optical gap in the spectrum and also the strongest collective transition. The bowl also has a high optical threshold, larger than 5 eV, but the intensity of the first significant transition is an order of magnitude weaker than in the ring. The relative intensities of the peaks, the fact that the first excitation is divided into two for the bowl, and the relative strength of the excitations in the 6-7 eV region, can all be used to distinguish the bowl isomer from the ring.

The spectra of the four three-dimensional isomers start at much lower energy and are more similar to each other, which is expected from their similar geometries. The fullerene isomer exhibits two peaks at 3.9 and 5.1 eV, with the second much stronger than the first one. Most of the strength concentrates above the ionization threshold (7.5 eV), and has a broad plateau starting at around 7 eV.
This is different from planar-like isomers, where an important fraction of the strength appears below 7 eV. Isomer (d) can be distinguished by the presence of a transition at quite low energy, 2.5 eV, as well as by the fragmentation into many states going up to 6 eV. Isomer (e) differs from the fullerene cage by the presence of a transition (labelled as B in the Figure) between the transitions that would be seen in the cage. The spectrum of isomer (f) is similar to that of the fullerene cage up to the second peak, but it is shifted down by about 0.3 eV. This is close to the borderline where the TDDFT energies are reliable. However, isomer (f) also has a third peak near 6 eV, in a region where there is a gap in the fullerene cage spectrum, and that difference would be definitive.

The benzene molecule, \( \text{C}_6\text{H}_6 \), was studied using the OCTOPUS code [146] and its predecessor code [163]. The results from the OCTOPUS code are shown in Figure 18. The main features are: (i) the narrow peak at about 7 eV, that corresponds to the transition between the \( \pi \) and \( \pi^* \) orbitals (also shown in the Figure), a characteristic of Carbon conjugated compounds, and (ii) the broad feature above 9 eV, which corresponds to the \( \sigma \rightarrow \sigma^* \) transition. The method works well for all organic molecules studied (see the OCTOPUS web page [146] for a data base).

18.3 Applications to biomolecules

Besides the spectacular advances over the last years in the characterisation of structural and dynamical properties of biomolecules by a combination of quantum mechanical and classical molecular mechanics methods, the theoretical understanding of the interaction of those molecules with external time-dependent fields is in its infancy in spite of the large amount of experimental work on photoactive molecules. In particular, processes related to vision and photosynthesis rely on a subtle interplay between optical absorption in the photoactive center and its decaying mechanism through the coupling to the internal vibrational modes of the molecule, including isomerization processes as well as coupling to the environment (supporting protein and solvent).

In this context the Green Fluorescent Protein (GFP) has been studied experimentally in various environments (in solution as well as in vacuo), and has been found to exhibit a rich and complex behavior that is the subject of much current debate. The measured optical absorption spectrum of the
wild type (wt) GFP shows two main resonances at 2.63 and 3.05 eV [165,166] (see Figure 19), that are attributed to two different thermodynamically stable protonation states of the chromophore (neutral and negative configurations of the chromophore, respectively). So far, ab initio quantum chemistry has not been able to provide satisfactory agreement with the spectroscopic data, and thus has not contributed too much to confirm or rule out various possible scenarios of photodynamics in GFP. A good description of the optical properties of the GFP photoreceptor has been achieved in recent work [167] using an approach combining a quantum-mechanical molecular-mechanics (QM-MM) method to obtain the structure with time-dependent density functional theory to treat the electronic excitations. The structures were optimized using a hybrid quantum mechanical-molecular mechanics (QM-MM) method [168,169] with a semiempirical hamiltonian [170] to describe the quantum subsystem. The QM region was formed by three amino-acid sequences, Ser65, Tyr66 and Gly67. The frontier between the QM and MM regions was treated within the H-link approximation. In this approach a hydrogen atom is included whenever the frontier between the QM and MM regions passes through a chemical bond. This H-link atom is forced during the minimization to be on the line along the frontier bond, and does not interact with the MM atoms. The optimized structure of the chromophore with the most important neighbor residues is shown in Figure 20. On the other hand, the anionic form of the chromophore was obtained by deprotonation of the Tyr66 and protonation of Glu222. The computed photoabsorption spectra of the GFP neutral and anionic chromophores, shown in Figure 19, are in excellent agreement with experiment assuming the presence of the two forms, protonated and deprotonated respectively, of the photo-receptor in an approximate 4:1 ratio. Furthermore, it can be seen in the inset of Figure 19 that light polarized along the x-direction is responsible for the lowest optical transition. The molecule is nearly transparent to visible light polarized along the other two orthogonal directions. GFP turns out to be a rather anisotropic molecule in the visible, a property that could be used to enhance the photo-dynamical processes in well oriented GFP samples for opto-electronic devices. The new approach developed holds great promise for future applications in biochemistry and biophysics as it is able to handle not only the optical response but also ultrashort femtosecond electron-ion dynamics. Preliminary calculations [171] for the optical spectra of the DNA basis is also in excellent agreement with available experimental data.
18.4 Local orbitals

A method has been derived [172] based on the description of the electronic wave functions using a linear combination of atomic orbitals (LCAO). Since the size of the LCAO basis is small, the scheme leads to matrices with a size substantially smaller than other methods. In that method, use is made of the SIESTA code [173,174] to compute the initial wave functions and the Hamiltonian matrix for each time step. In the SIESTA code the core electrons are replaced by norm-conserving pseudopotentials, and the basis set is a linear combination of numerical atomic orbitals (NAOs), constructed from the eigenstates of the atomic pseudopotentials.

To calculate the linear optical response, the explicit time evolution of the wave functions is followed. A bounded system in a weak electric field is first considered, and the ground state of the system is calculated using standard time-independent DFT. This is achieved in practice by including a perturbation $\Delta H = -E \cdot x$, and setting a small value for the field. Then, the field is switched off at time $t = 0$ and the occupied Kohn-Sham eigenstates are propagated in time by solving the time-dependent Kohn-Sham equation with the ALDA for exchange-correlation [172].

The calculation of the optical response of Na$_8$ is a difficult test for codes that use localized orbitals because of the delocalized electron density of this cluster. The basis set used by Tsolakidis includes 13 NAOs per atom: two radial shapes to represent the $3s$ states plus a polarization $p$ shell with confinement radii $r_s = r_p^{pol}$ equal to 12.2 a.u., and two additional $3p$ and $3d$ shells with confinement radii $r_p = r_d$ of 10.0 a.u. The shape of the calculated imaginary part of the linear dynamical polarizability is in good agreement with other calculations [39] and with experiment [51]. However, the maximum of the plasmon is obtained at 2.8 eV, that is, the peak is shifted by 0.27 eV to higher energies with respect to experiment. This shift seems to be related to the extension of the LCAO basis: the more confined the orbitals, the larger the shift.

C$_{60}$ is characterised by strong electron-electron interactions due to the confinement. 13 NAOs were used for this cluster: two different radial shapes for the description of the $2s$ states, another two for the $2p$, plus an additional shell of $d$ orbitals. The calculated spectra show a small dependence of
the confinement radii. The dipole strength function obtained from the time evolution of the dipole moment is shown in Figure 21, for energies up to 60 eV. The main features of the spectrum are the low energy transitions arising from the $\pi$ electrons and the $\sigma$ and $\pi$ transitions in the region of 14-27 eV. In the low energy region, peaks appear at 3.5, 4.4, 5.4, and 5.8 eV, which agree well with those observed in the experiments [175]. The integration of the dipole strength over energy gives a sum rule strength of 223.8, while an exact fulfillment of the sum rule should give 240. The sum rule is then satisfied up to 93.2%, and this reflects the incompleteness of the basis set, which fails to reproduce some of the high energy excitations.

The nonperturbative nature of the method allows, for large values of the applied field, to obtain nonlinear polarizabilities. Tsolakidis et al [172] also developed a method for the calculation of the imaginary part of the integrated frequency-dependent second-order nonlinear polarizability. The advantage of the explicit-time method is that it uses the same operations as in the linear case. The disadvantage is that, unlike the linear case where each Fourier component is independent, the nonlinear response depends upon the detailed spectrum of the applied field. The method developed is valid for a field which is a step function, and it was applied to $C_{60}$.

19. Assessment of exchange-correlation functionals for the calculation of optical properties

When the excitation energies are obtained from the time-dependent density, that is, by solving the time-dependent Kohn-Sham equations (see eq. (30)), an approximated time-dependent exchange-correlation potential $V_{xc}(r,t)$ has to be used. This potential is expected to be much simpler to model than the exchange-correlation kernel $K_{xc}[n](r,t,r',t')$ which is required in the other formulation, that is, when the excitations are obtained from the position of the poles of the KS linear response function.
The simplest and most commonly used approximation is again the adiabatic LDA (or ALDA), in which the static LDA exchange-correlation potential is used in the time-dependent Kohn-Sham equations, but evaluated at the time-dependent density, that is

$$ V_{xc}^{ALDA}(r,t) = V_{xc}^{LDA}(n(r,t)) \quad (92) $$

One can also start with the static Generalized Gradient Approximation (GGA) [176,177]

$$ E_{xc}^{GGA} = \int d^3 r \, n(r) \varepsilon_{xc}^{GGA}(n(r), \nabla n(r)) \quad (93) $$

where $\nabla n(r)$ is the gradient of the density at the point $r$, and $\varepsilon_{xc}^{GGA}$ is an analytic function of $n(r)$ and $\nabla n(r)$ with some free parameters that are either fitted to experiment or determined by fulfilling some exact sum rules. Following then the same reasoning it is straightforward to construct adiabatic GGA potentials. Unfortunately, the onset of absorption calculated either with the adiabatic LDA or GGA functionals are typically below the observed ones (by several eV in the case of atoms). This problem is once more related to the wrong asymptotic behavior of the effective Kohn-Sham potential, which goes exponentially to zero instead of having the correct behaviour $-1/r$ for neutral systems. This is due to the insufficient correction of the self-interaction part of the Hartree potential. As a simple way to correct the asymptotic part of the adiabatic potential one can use the adiabatic approximation of van Leeuven and Baerends (known as LB94) [178]. These authors applied the Becke GGA construction [176] not to the derivation of the exchange energy functional (like in Becke’s original work), but to the modelling of the exchange-correlation potential directly. By imposing the correct asymptotic behaviour to the exchange-correlation potential, much better ionization potentials, and energy eigenvalues in general, have been obtained. However, the high-lying excitation energies calculated with the LB94 potential are usually overestimated for small molecules, and the performance for low-lying states is less accurate than for ALDA [179].

To overcome some of the difficulties encountered when trying to write $V_{xc}$ as an explicit functional of the density, orbital-dependent xc-functionals have been introduced. Those functionals are written explicitly in terms of the Kohn-Sham orbitals, albeit remaining implicit density functionals due to the Runge-Gross theorem (see Section 4 and ref. [27]). The exact-exchange (EXX) functional,
which is a typical member of this family, is obtained by expanding the action functional \( A_{xc} \) in powers of \( e^2 \) (\( e \) is the electronic charge), and retaining the lowest order term only, that is, the exchange term. This is given by the Fock integral

\[
A_{xc}^{EXX} = -\frac{1}{2} \sum_{j,k} \int dt \int d^3r \int d^3r' \frac{\psi_j^*(r',t)\psi_k^*(r',t)\psi_j(r,t)\psi_k(r,t)}{|\mathbf{r} - \mathbf{r}'|}. \tag{93}
\]

From this action functional one determines the local Kohn-Sham potential by a series of chain rules for functional derivatives. The procedure is called the optimized potential method (OEP), and the derivation of the time-dependent version of the OEP equations [42] is very similar. The final equation that determines the EXX potential has the form of an integral equation, and its solution poses a hard numerical problem. By performing an approximation first proposed by Krieger, Li and Iafrate [41] it is possible to obtain a semianalytical solution of the integral equation. The kernel corresponding to the optimized effective potential (OEP) was presented in equation (64). The self-interaction corrected Local Density Approximation (or SIC-LDA) [180] is another example of an orbital-dependent functional

\[
E_{xc}^{SIC} = E_{xc}^{LDA}[n_\uparrow(r), n_\downarrow(r)] - \sum_\sigma \sum_{i=1}^N E_{xc}^{LDA}[\psi_\sigma^a(r)]^2 - \frac{1}{2} \sum_\sigma \sum_{i=1}^N \int d^3r d^3r' \frac{\psi_\sigma^a(r)^2\psi_\sigma^a(r')^2}{|\mathbf{r} - \mathbf{r}'|}. \tag{94}
\]

In this functional, \( \sigma \) is the spin index \((\uparrow, \downarrow)\). The first term in the functional is the LDA approximation, in its spin-dependent version, the second term subtracts the self-interaction part of the exchange-correlation functional, and the last term exactly cancels the self-interaction part of the Hartree term (that is the spurious interaction of an electron with itself that appears in the classical coulomb interaction expressed in terms of the total electron density). The time-dependent generalization of \( V_{xc}^{SIC-LDA} \) is immediate.

### 19.1 Metal clusters

The performance of the adiabatic \( V_{xc}(\mathbf{r},t) \) functionals discussed above has been compared for small Sodium and Silane molecules [145]. All the calculated optical spectra of \( \text{Na}_2 \) (LDA, GGA, EXX,
SIC-LDA and LB94) are quite similar, regardless of the exchange-correlation potential used. Those spectra show three peaks in the 2-5 eV range, and compare quite well with experiment, although the DFT peaks are all shifted towards higher energies by amounts ranging from 0.2 to 0.4 eV. Since the electronic transition energies can be expressed (see eq. (57))

\[
\Omega_{vc} = \varepsilon_v - \varepsilon_c + \left(\psi_v \psi_c \left| \frac{1}{r_1 - r_2} \right| \psi_v \psi_c \right) + \Delta_{xc},
\]

(95)

the shift can be understood as resulting from the competition between the Coulomb repulsion contribution to the response and the electron-hole attraction in the exchange-correlation part. For a given \(v \rightarrow c\) transition, the adiabatic LDA approximation introduces only an effective static attractive electron-hole interaction (the expressions are more complicated for other kernels)

\[
\Delta_{xc} = \int d^3r \psi_v^*(r) \psi_c(r) \frac{\partial V_{xc}(r)}{\partial n} \psi_v^*(r) \psi_c(r),
\]

(96)

but it is clear that the effective attractive interaction is not complete. Dynamical effects may be needed in the kernel to recover this minor effect. Also, temperature effects may introduce a broadening of the spectrum as well as a shift of the peaks to lower frequencies [140,141]. The functional giving the best results, although by a small margin, is EXX, while the strongest departure from the experiment is found for LB94.

For \(\text{Na}_4\), shown in Figure 22, all the calculations yield similar spectra. The spectrum consists of three peaks in the 1.5-3.5 eV range, and a broader feature around 4.5 eV. The comparison with the experimental peak positions is quite good, although the calculated peaks appear, again, shifted to higher energies by \(\approx 0.2\) eV. The deviation of the LB94 is a little bit larger. In general, the errors in the calculations with all these functionals are larger for the high energy peaks, which involve transitions to states near the ionization threshold. The figure also contains the results of a GW quasiparticle many-body calculation including excitonic effects [181] (see Section 21).

### 19.2 Silanes
The two simplest hydrogen-terminated silicon clusters, Silane (SiH\textsubscript{4}) and Disilane (Si\textsubscript{2}H\textsubscript{6}), pose a much harder challenge that the alkali clusters, due to the presence of \textit{p} electrons and also due to the hydrogen atoms. As expected, the different exchange-correlation functionals lead to dissimilar results [145]. The HOMO-LUMO gaps obtained for SiH\textsubscript{4} with the different functionals are: 8.10 eV (LDA), 8.12 eV (GGA), 8.40 eV (LB94), 7.70 eV (SIC-LDA), and 8.77 eV (EXX). The differences between them are not large, although it is worth noticing the the smallest value is obtained for SIC, and the largest ones for LB94 and EXX. All those gaps are, however, smaller that the value of 13.0 eV obtained in a GW calculation [182]. For Si\textsubscript{2}H\textsubscript{6} the HOMO-LUMO gaps are: 6.76 eV (LDA), 6.80 eV (GGA), 6.58 eV (LB94), 5.98 eV (SIC) and 7.17 eV (EXX), and again the variations are not large. However, the main difference between those methods is a nearly rigid shift of the spectrum of the LDA and GGA energy eigenvalues with respect to LB94 and EXX. The upwards shift leads to lower electronic binding energies. The SIC spectrum is also shifted, but much less.

The experimental absorption spectrum of silane [183], given in Figure 23, has three peaks between 8 and 12 eV, followed by a much broader feature at higher energies. The peaks derive from a Jahn-Teller splitting of the triply degenerate \(2\text{t}_2 \rightarrow 4s\) transition. The spectra obtained with the LDA and GGA functionals (upper panel in the Figure) are quite similar to each other and the onset of absorption is underestimated by around 1 eV with respect to experiment. On the other hand, the SIC spectrum (given in the lower panel) is unphysically shifted to lower energies, and its first peak is split. The shifts of the SIC, LDA and GGA spectra could be anticipated from the low HOMO-LUMO gaps. The LB94 and EXX functionals behave quite well: the onset of absorption is now correct and the error in the position of the first three peaks is reduced by a factor of 2 from the LDA or GGA results. The LDA, GGA, LB94 and EXX spectra of disilane (Si\textsubscript{2}H\textsubscript{6}) are all very similar and consist of five peaks in the interval 7-12 eV, followed by a broader feature at higher energies. The overall comparison with experiment is slightly better than for silane. The SIC-LDA functional yielded again a quite unreasonable spectrum.

20. Nonlinear processes
20.1 Clusters in strong laser fields

Progress in laser technology has opened new lines of research in the domain of non-linear cluster dynamics. Lasers offer an ideal tool for spanning various dynamical regimes, ranging from the linear regime with plasmon-dominated dynamics (already discussed in previous Sections), to the semi-linear regime of multi-photon absorption processes [184,185] and the strongly non-linear regime of Coulomb explosion [186,187]. From the theoretical side, only theories based on DFT have been able to deal with such different situations and dynamical regimes for clusters. Those calculations [188] have exploited the numerical experience acquired in Nuclear Physics.

Let us sketch the various steps appearing in the response of highly-excited metal clusters. In addition to the irradiation by intense femtosecond laser pulses [189], one can consider another class of rapid, intense, excitations: collisions with energetic highly-charged ions [190]. In both cases the excitation takes place in times between tens of femtoseconds (fs) down to below 1 fs. This time is directly comparable to characteristic time scales of the valence electron cloud, and consequently the cluster response is primarily of electronic nature. The first phase of the reaction is a direct emission of electrons and an oscillation of the collective plasmon. This first phase is characterized by time scales of the order 1-10 fs. In a second stage, still of purely electronic nature, damping of the collective electronic motion takes place, both by means of Landau-like damping (that is, excitation of resonances in the continuum) and by electron-electron collisions. The time scales associated to these effects are variable depending on the cluster size (Landau-like damping) and the deposited excitation energy (electron-electron collisions). Landau-like damping takes 10-20 fs and collisional effects around 10-100 fs. After that, the electronic degrees of freedom slowly couple to the ionic motion, and may lead to the explosion of the charged cluster on long times, of several hundred fs. Two mechanisms operate here: the first one is the coulombic repulsion due to the net charge of the cluster following ionization, and the second corresponds to energy exchanges between the hot electron cloud and the still cold ions. The two effects interfere constructively to activate ionic motion and to lead to evaporation, fission or fragmentation. Thermal evaporation of electrons proceeds on a very long time
Two examples are now considered, in order to illustrate the various stages of the excitation and response of metal clusters in the non-linear regime. The first example places the focus on the electronic response. Figure 24 represents the first stage in the response of Na$_{93}^+$ irradiated by an intense laser pulse [134], that is, the electronic response. The cluster structure is treated in the jellium approximation and the laser pulse is modeled by a ramp pulse (trapezium shape) with a total duration of 100 fs. The intensity is $I = 10^{10}$ W/cm$^2$, and the photon frequency, $\hbar \omega = 3.1$ eV, is slightly above the Mie resonance for this cluster. The response depends crucially on the actual laser frequency [188,191]. For laser frequencies sufficiently far away from the plasmon resonance, the dipole response follows closely the pulse profile and disappears when the laser pulse profile vanishes. On the contrary, for laser frequencies close to the Mie resonance, the laser may attach the resonance. This results in a sizable electron emission, and the dipole response survives the laser pulse as it generated a true eigenfrequency of the system. The example considered in Figure 24 corresponds to a situation in which the plasmon actually comes into play during the process. For the first 50 fs, the laser pulse remains above resonance and the electronic dipole moment $D(t)$ follows the profile of the pulse (see the upper panel in the Figure). The laser intensity is still enough to induce the ionization of the cluster. The charge deficit makes the electronic cloud of the cluster more compressed (the ionic background does not change in the model) and this shifts the plasmon resonance towards higher frequencies, and thus closer to the laser frequency. From about 50 fs on, the Mie plasmon couples resonantly with the laser, and this leads to a substantial increase in ionization. The process reaches a peak until the violent electron emission produces a further blueshift of the plasmon frequency that detunes the plasmon from the laser. Still, even after the pulse has been switched off and electron emission has levelled off, the electron cloud continues performing collective oscillations at the actual plasmon frequency of the system (that is, the frequency is consistent with the net charge of the cluster).

This example illustrates the role of the plasmon resonance in triggering ionization. For the moderately short pulses considered, the ion positions remain practically frozen and do not interfere
with the ionization process. However, this is not the case when longer pulses are considered. Indeed, experiments [187] in Platinum clusters suggest that the highly-charged cluster rapidly undergoes a Coulomb expansion, with a time scale of 100-500 fs. An interference can thus occur between the laser pulse and the ionic motion, which may enhance the ionization.

A second example, the excitation of $\text{Na}^{+}_{41}$ subjected to a long laser pulse (240 fs) of frequency $\hbar \omega_{\text{laser}} = 2.86 \text{ eV}$, shows how the ionic motion can interfere with the excitation process. The excitation of this cluster has been simulated using the TDLDA [192]. The results are presented in Figure 25. Explicit account of the ions is needed, and the ion-electron interaction was modeled with pseudopotentials. The third panel, giving the number of electrons emitted, $N_{\text{esc}}$, shows that ionization takes place in several steps. Again, in a first phase, lasting for about 80 fs, the response is fully electronic, and is characterized by a low ionization. But the net charge of the cluster shifts the plasmon resonance upwards until it comes into resonance with the laser. This results in a sudden increase in ionization around 100 fs, leaving the cluster in a state with a net charge $5^+$. Up to that stage, the situation is similar to the previous case of $\text{Na}^{+}_{93}$. From then on, ionization proceeds at a slower pace until another burst of electrons shows up around 250 fs, stripping again about 5 electrons. The lowest panel of the Figure gives the electric dipole signal $D(t)$. It is clear that large slopes in ionization ($N_{\text{esc}}$) are correlated with large dipole amplitudes, which again reflects resonant conditions.

A relation between the two observables is observed by plotting in the second panel the instantaneous plasmon frequency $\omega_{\text{res}}(t)$, calculated at each time $t$ for the instantaneous structure and charge of the cluster. The laser frequency is the dashed horizontal line in the same panel. The correlation between large slopes in $N_{\text{esc}}$ and resonant conditions is noticeable. The first coincidence at time 100 fs reflects the blueshift of the plasmon due to the first stage of ionization and corresponds to an electronic effect. It also triggers the time at which a sizeable Coulomb expansion of the ionic distribution starts (see also uppermost panel). And it is noteworthy that this occurs rather soon (about 50 fs) after the violent initial charging. The Coulomb expansion in turn leads to a redshift of the
resonance (see equation (9)), which is responsible for the second coincidence at 230 fs. The system thus acquires a much higher charge state and ends up in a violent Coulomb explosion.

Other nonlinear phenomena related to the coupled electron-ion dynamics correspond to the selective dissociation of molecules, isomerization, and the possibility of having an inverse Landau damping process, that is, an electron-hole excitation decaying by emitting a plasmon [193].

20.2 High harmonic generation

By irradiating an atom, a molecule or a surface with a high intensity laser, an electron may absorb several photons and then return to its original state by emitting a single photon. The emitted photon will have a frequency that is a multiple number of the laser frequency. This process is known as high harmonic generation. Since the emitted high energy photons maintain a high coherence, they can be used as a source for X ray lasers. Figure 26 shows the harmonic spectrum of the Helium atom. The experimental data, from Miyazaki and Sakai [194], is represented by the squares. The solid line gives the theoretical results [195] obtained from the TDDFT using the EXX (exact exchange) functional. The spectrum shows a series of peaks that first decrease in amplitude, until a plateau is reached that extends to very high frequency. The frequencies of the peaks are odd multiples of the laser frequency. The even multiples are dipole forbidden by symmetry. All theoretical approaches based on perturbation theory would produce a harmonic spectrum that decays exponentially. TDDFT, on the other hand, reproduces well the measured intensities.

High harmonic generation can, as indicated above, be used as a source of soft X rays lasers. To this end, one should optimize the laser parameters, frequency, intensity, etc, in order to increase the intensity of the emitted harmonics and to extend the plateau as farthest as possible. TDDFT “computer experiments” can be helpful for this task. Erhard and Gross [196] have modelled the irradiation of H atoms with lasers of a common frequency and different intensities. They found that the amplitude of the harmonics increases as the intensity of the laser increases, until a maximum amplitude is reached for a given intensity. Beyond that laser intensity, the amplitude of the harmonics decreases because the probability for ionization becomes substantial.
21. Many body techniques: GW quasiparticles

We have seen above (Section 5) that the eigenvalues of the Kohn-Sham equations of DFT cannot be interpreted as electron removal energies. A successful development to compute excitations in electronic systems has been a first-principles self-energy approach in which the quasiparticle (qp) energies are determined directly by calculating the contribution of the dynamical polarization of the surrounding electrons. There are no parameters in this theory and the quasiparticle energies and wavefunctions are determined by solving a Schrödinger-like equation

\[
(T + V_{\text{ext}} + V_H)\psi_{i\text{qp}}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; E_i) \psi_{i\text{qp}}(\mathbf{r}') = E \psi_{i\text{qp}}(\mathbf{r})
\]

where \(T\) is the kinetic energy operator, \(V_{\text{ext}}\) is the external potential due to the ions, \(V_H\) is the Hartree potential of the electrons and \(\Sigma\) is the self-energy operator where all the many-body exchange and correlation effects are included. The self-energy operator describes an effective potential on the quasiparticle resulting from the response of the other electrons in the system. In general \(\Sigma\) is nonlocal, energy dependent and non-Hermitian, with the imaginary part giving the lifetime of the quasiparticles. In practical implementations (the so called GW approximation [197-199]), the self-energy operator is taken to be the first order term in a series expansion in terms of the screened Coulomb interaction \(W\) and the dressed Green’s function \(G\) of the electron as

\[
\Sigma(\mathbf{r}, \mathbf{r}'; E) = \frac{i}{2\pi} \int d\omega \ e^{-i\omega \delta} G(\mathbf{r}, \mathbf{r}'; E - \omega) W(\mathbf{r}, \mathbf{r}'; \omega)
\]

where \(\delta\) is a positive infinitesimal. Vertex corrections are not included in this approximation [197-199]. The quasiparticle energy is usually computed within the framework of DFT as

\[
E_i = \epsilon_i^{\text{DFT}} + \langle \psi_i^{\text{DFT}} | \Sigma(E_i) - V_{\text{xc}}^{\text{DFT}} | \psi_i^{\text{DFT}} \rangle
\]

where \(V_{\text{xc}}^{\text{DFT}}\) is the exchange-correlation potential within DFT and \(\epsilon_i^{\text{DFT}}\) and \(\psi_i^{\text{DFT}}\) are the corresponding orbital energies and wavefunctions. Two major components of the theory are the time-ordered one-electron Green’s function

\[
G(\mathbf{r}, \mathbf{r}'; E) = \sum_i \frac{\psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')}{E - E_i - i\delta}
\]
(δ = 0⁺ for $E < \mu$, and δ = 0⁻ for $E > \mu$, where $\mu$ is the Fermi energy) and the dynamically screened Coulomb interaction

$$W(r, r'; E) = \frac{1}{\Omega} \int d\mathbf{r} \varepsilon (\mathbf{r}, \mathbf{r}'; E) \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

where is the volume and $\varepsilon (\mathbf{r}, \mathbf{r}'; E)$ is the time-ordered dielectric response function of the system. In general, the Hedin’s procedure is a self-consistent scheme to first order in $W$. The general equations are (the numbers stand for spatial and temporal coordinates and $v$ for the bare coulomb interaction),

$$\Sigma(12) = i \int G(13) \Gamma(324) W(41) d(34)$$

$$W(12) = v(12) + \int v(13) P(34) W(42) d(34)$$

$$P(12) = -i \int G(13) G(41) \Gamma(324) d(34)$$

$$\Gamma(123) = \delta(12) \delta(13) + \int \frac{\delta \Sigma(12)}{\delta G(45)} G(46) G(75) \Gamma(673) d(4567).$$

The polarizator $P(12)$ is the time-ordered counterpart of the retarded response functions. The main idea of the GW approach is to start the iteration of these equations neglecting vertex corrections, that is, $\Gamma(123)$ is assumed to be a diagonal operator. In this way the polarizator and self-energy operators read as $P = iGG$ and $\Sigma = i GW$, explaining why the approximation is called GW. Adding on top of these equations the Dyson equation for the Green function

$$G = G^{DFT} + G^{DFT} \Sigma G$$

where $G^{DFT}$ is the DFT Green’s function obtained from the Kohn-Sham orbital energies and wave functions, we can see that, even at the GW level, we have a many-body self-consistent problem. Most GW applications do this selfconsistent loop by varying the energy of the quasiparticle but keeping fixed the wavefunction, equal to the DFT wavefunction.

Using standard many-body techniques one can write the exchange-correlation energy and get from it the exchange-correlation potential. In this way we can extract an exact equation for the exchange-correlation potential in terms of the exchange-correlation part of the self-energy operator [200]

$$\int dr_1 V_{xc}(r_1) \int dE G_0(r_1, r_1, E) G(r_1, r, E) = \int dr_1 \int dr_2 \int dE G_0(r_1, r_1, E) \Sigma_{xc}(r_1, r_2, E) G(r_2, r, E).$$
If only the exchange term is kept in $\Sigma$ and $G$ is replaced by $G_0$ we obtain the local potential in the Hartree-Fock approximation. When applying this equation to bulk Si it is found that the overlap between the quasiparticle wavefunctions and the LDA-wavefunction is higher than 99 %, what justifies choosing the DFT Green’s functions in the GW procedure. However, this agreement is less satisfactory for II-VI or III-V semiconductors with semicore levels close to the valence complex and for transition metal systems. In those cases it is necessary to iterate the GW equations to get good quasiparticle energies and wavefunctions, and from these the corresponding exchange-correlation potential. The formalism can be extended to the time-dependent domain in order to derive correlation contributions to the time-dependent exchange-correlation potential [201]. The inclusion of vertex corrections, that is the inclusion of $\Gamma$ for $P$, can be achieved through a second iteration of Hedin’s equations. For a review comparing many-body approaches and TDDFT schemes, see ref. [3].

The quasiparticle energies of small closed-shell Sodium and Potassium clusters have been calculated [33] using a spherical jellium model description of the cluster structure. The results for Na$_{20}$ are compared in Table 6 with the DFT energy eigenvalues. The quasiparticle energies of the occupied states (shells 1$s$, 1$p$, 1$d$ and 2$s$) are more negative than the LDA eigenvalues. The opposite occurs for the quasiparticle energy $E_{1f}$ of the lowest unoccupied shell, and consequently the energy gap is larger in the GW calculation. The result found for bulk semiconductors and insulators is similar [202]. As expected, the absolute value of the highest occupied quasiparticle energies of the Na and K clusters are closer to the experimental ionization potentials than the LDA Kohn-Sham eigenvalues [33]. It is useful to notice that a DFT calculation using the nonlocal WDA for exchange-correlation effects has been able to give Kohn-Sham energy eigenvalues of occupied states in very good agreement with the quasiparticle energies [32]. The WDA results are given in the last column of Table 6. The description of the ionization potentials of the Na and K clusters, as approximated by the absolute value of the HOMO eigenvalue, becomes also substantially improved with respect to the LDA. The improvement is due to the more accurate account of the asymptotic part of the exchange-correlation potential.
The results of a GW calculation of the optical spectrum of Na₄ by Onida et al [181] including the rhombic structure of the cluster are given in Figure 22. The LDA energy eigenvalues and orbitals form the input for the evaluation of the RPA screened Coulomb interaction $W$ and the self-energy $\Sigma$. The quasiparticle energies are then evaluated in first order perturbation theory in $\Sigma - V_x$. The GW corrections to the energies of the empty states are between 0.75 and 0.9 eV. The HOMO and the lowest occupied state are lowered by 1.55 and 1.4 eV, respectively. This leads to a HOMO-LUMO gap of 3.0 eV, to be compared to the small LDA gap of 0.55 eV. These large corrections are expected for a system in which screening is weak. The calculation of Onida et al also includes excitonic effects, that is the binding interaction between the electron and hole quasiparticles that occurs when electron-hole pairs are created, as in optical excitations. Starting with the quasiparticle energies, the excitonic effects are computed from an effective two-particle interaction which includes the screened electron-hole interaction and also an unscreened exchange term [203]. These excitonic effects are expected to be large when screening is weak and, in fact, absorption occurs in Na₄ at energies substantially smaller than the quasiparticle gap. In summary, the Figure reveals good agreement with experiment for both the positions (within 0.2 eV) and the relative oscillator strengths of the main peaks of the photoabsorption spectrum. The final results are in similar agreement with experiment than the calculations based on TDLDA discussed in Section 19.1 above, and Figure 22 puts in evidence this comparison.

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Figures Captions

Fig. §.1

Experiment for measuring the photoabsorption cross section of metallic clusters. The collimated beam is ionized with ultraviolet light (UV) and the ionized clusters enter a quadrupole mass analyzer (QMA). A counterpropagating laser beam heats up the clusters. Some clusters evaporate atoms and are removed from the original beam, and the ratio between the number of clusters of a given size arriving at the detector with and without laser excitation gives the cross section. From ref. [4], K. Selby, M. Vollmer, J. Masui, V. Kresin, W. A. de Heer and W. D. Knight, Phys. Rev. B 40, 5417 (1989), with permission from the American Physical Society @ 1989.

Fig. §.2

Schematic representation of the collective dipole spectrum of Sodium clusters obtained in linear response theory. The strenght function $S(\omega)$ is plotted as the percentage of the total dipole strength $m_1$, normalized to 100% (see equations (7) and (13)). The spectrum in the lowest pannel represents the classical limit for a large metallic sphere, where all the strength is concentrated in the surface plasmon of frequency $\omega_{\text{Mie}}$ and the volume plasmon (of frequency $\omega_{\text{pl}}$) has zero strength. For finite clusters the surface plasmon is red-shifted and its missing strength is distributed over the reminder of the strongly fragmented volume plasmon. From ref. [6], M. Brack, Rev. Mod. Phys. 65, 677 (1993), with permission from the American Physical Society @ 1993.

Fig. §.3

Imaginary part of the dynamical polarizability (per electron) of Na$_{20}$. The calculations employed the spherical jellium model and the TDLDA. Dotted and continuous curves correspond to using the non-
interacting \( (\chi_s) \) and fully interacting \( (\chi) \) dynamical susceptibilities, respectively. Transitions are broadened to simulate temperature effects. From ref. [26], A. Rubio, J. A. Alonso, X. Blase and S. G. Louie, Int. J. Mod. Phys. B 11, 2727 (1997), with permission from World Scientific Publ. Company @ 1997.

Fig. §.4

Calculated (LDA,WDA) [26,49] and experimental [53] photoabsorption cross sections (per electron) of Na\(_{20}\) in the spherical jellium model. Arrows mark the positions of observed peaks [56]. From ref. [26], A. Rubio, J. A. Alonso, X. Blase and S. G. Louie, Int. J. Mod. Phys. B 11, 2727 (1997), with permission from World Scientific Publ. Company @ 1997.

Fig. §.5

Calculated photoabsorption cross sections, per electron, of Na\(_N^-\) cluster anions. The clusters are described by the spherical jellium model. The nonlocal WDA approximation was used for exchange and correlation. The arrows mark the binding energy of the highest occupied molecular orbital. From ref. [26], A. Rubio, J. A. Alonso, X. Blase and S. G. Louie, Int. J. Mod. Phys. B 11, 2727 (1997), with permission from World Scientific Publ. Company @ 1997.

Fig. §.6

Fig. §.7

Calculated photoabsorption cross section of Na$_{21}^+$ in the jellium (upper panel) and SAPS (lower panel) models. Dashed and continuous curves correspond to LDA and nonlocal WDA treatments of exchange and correlation. The arrows indicate the experimental position of the plasmon resonance. From ref. [26], A. Rubio, J. A. Alonso, X. Blase and S. G. Louie, Int. J. Mod. Phys. B 11, 2727 (1997), with permission from World Scientific Publ. Company @ 1997.

Fig. §.8

Photoabsorption cross section per electron for Na$_{10}$ in the ground state configuration (the structure is given in the inset). The dashed line is from the SAPS model. The full symmetry is taken perturbatively in the calculation for the continuous line. Adapted from ref. [86], W. D. Schöne, W. Ekardt and J. M. Pacheco, Phys. Rev. B 50, 11079 (1994), with permission from the American Physical Society @ 1994.

Fig. §.9

Calculated photoabsorption cross section of RbK$_{19}$, K$_{20}$ and NaK$_{19}$. From ref. [93], C. Yannouleas, P. Jena and S. N. Khanna, Phys. Rev. B 46, 9751 (1992), with permission from the American Physical Society @ 1992.

Fig. §.10

Electron density (continuous line) and positive background density (dashed-dotted line) as a function of distance to the cluster center in a simple continuous model for [C$_{60}$Na$_{93}$]$^+$. Adapted from ref. [105],

Fig. §.11

Calculated photoabsorption cross section, per electron, of \( [C_{60}Na_{93}]^+ \).

Fig. §.12

Photoabsorption cross section of \( \text{Li}_8 \). The dashed line is for the Jellium model and the continuous line is obtained with full account of the geometrical structure. The centroid of the experimental resonance is indicated by the arrow.

Fig. §.13

Averaged photoabsorption cross section of two different isomers of the \( \text{Si}_4 \) and \( \text{Si}_6 \) clusters, shown by the continuous line. The independent-particle spectra (dotted curves) have been included for comparison. All the spectra have been broadened by 0.1 eV. The cluster geometries are included in the insets, and some bond lengths are given in Å. From ref. [108], A. Rubio, J. A. Alonso, X. Blase, L. C. Balbás and S. G. Louie, Phys. Rev. Lett. 77, 247 (1996), with permission from the American Physical Society @ 1996.

Fig. §.14

Calculated and experimental absorption spectra of Sodium clusters. (a) Absorption spectra from the difference of Kohn-Sham eigenvalues. The other plots show spectra calculated form equation (61)
(panel b), equation (60) (panel c), and equation (59) (panel d). All calculated spectra are broadened by 0.06 eV to simulate finite temperature. The experimental spectra are adapted from references [51,120-122]. From ref. [39], I. Vasiliev, S. Ögut and J. R. Chelikowsky, Phys. Rev. Lett. 82, 1919 (1999), with permission from the American Physical Society @ 1999.

Fig. §.15

The symmetric fission of Na$_{18}^{3+}$ illustrated by plots of the ionic distribution (upper right) and equidensity plots of the electron density (middle right) at various stages indicated over the fission barrier (lower right). The left side shows the calculated optical response at some of those stages. From ref. [134], J. A. Alonso, M. Barranco, F. Garías, P. G. Reinhard and E. Suraud, E., in Fission Dynamics of Atomic Clusters and Nuclei, J. da Providencia, D. M. Brink, F. Karpechine and F. B. Malik (editors.), World Scientific, Singapore (2001), p. 163, with permission from World Scientific @ 2001.

Fig. §.16

Comparison of theoretical (histograms) and experimental (solid curves) [142] photoabsorption cross sections of Na$_3^+$ at 100 K (panel a), Na$_5^+$ at 100 K (panel b), Na$_3^+$ at 300 K (panel c), Na$_9^+$ at 100 K (panel d), and Na$_3^+$ at 450 K (panel e). Insets in panel (a) indicate constant density contour plots corresponding to electronic orbitals relevant for the discussion of the spectrum (see text). The contour plots in panels (d) and (e) correspond to the total electron density and reflect the shape of the cluster. Insets on the upper right sides of panels (b), (c), (d) and (e) give the oscillator strength for the cluster structures shown on the left side. From ref. [141], M. Moseler, H. Häkkinen and U. Landman, Phys. Rev. Lett. 87, 053401 (2001), with permission from the American Physical Society @ 2001.
Fig. §.17


Fig. §.18

Optical absorption of the benzene molecule calculated with the OCTOPUS code. Experimental result are from Koch [164]. The bottom panel shows $\pi$ and $\pi^*$ Kohn-Sham orbitals. Transitions between these two states are responsible for the large absorption peak at 7 eV. From ref. [146], M. A. L. Marques, A. Castro, G. F. Bertsch and A. Rubio, Computer Phys. Commun. 151, 60 (2003), with permission from Elsevier @ 2002.

Fig. §.19

Computed photoabsorption cross section of the neutral (thick solid line) and anionic (thick dashed line) chromophores. For comparative purposes the anionic results have been divided by 4. Experimental results at 1.6 K (thin solid lines) [165] and room temperature (crosses) [166] are also given. The inset shows a decomposition of the calculated spectrum of the neutral chromophore in the three directions, showing the inherent anisotropy of the green fluorescent proteine molecule. From ref. [167], M.A.L Marques, X. López, D. Varsano, A. Castro, and A. Rubio, Phys. Rev. Lett. 90, 258101 (2003), with permission from the American Physical Society @ 2003.

Fig. §.20

Optimized structure of the neutral chromophore and its closest charged residues inside the green fluorescent protein (GFP): His148, Arg96 (positive) and Glu222 (negative) From ref. [167], M.A.L
Fig. §.21


Fig. §.22

Averaged dipole strength of Na$_4$. The curve labelled exp shows the experimental photodepletion spectrum of Wang et al [51], GW shows the results of a many-body calculation including self-energy and excitonic effects [181], and PBE indicates the results of GGA calculations with the functional of Perdew, Burke and Ernzerhof [177]. The other curves (LDA, EXX, SIC-LDA and LB94) correspond to calculations with functionals explained in the text. The geometrical structure of Na$_4$ is shown in the inset. From ref. [145], M. A. L. Marques, A. Castro and Rubio, A., J. Chem. Phys. 115, 3006 (2001), with permission from the American Institute of Physics @ 2001.

Fig. §.23

Averaged dipole strength of SiH$_4$. The experimental curve (exp) is from Itoh [183]. PBE indicates the results of GGA calculations with the functional of Perdew, Burke and Ernzerhof [180]. The other curves (LDA, EXX, SIC-LDA and LB94) correspond to calculations with functionals explained in the text. The geometrical structure of SiH$_4$ is shown in the inset. From ref. [145], M. A. L. Marques, A.
Fig. §24


Fig. §25

TDLDA simulation of the excitation of $\text{Na}_{41}^+$ with a laser of frequency $\hbar \omega_{\text{laser}} = 2.86 \text{ eV}$, intensity $I = 9 \times 10^9$ W/cm$^2$ and pulse length 240 fs. From top to bottom: global extension of the ionic distribution in $z$-(along laser polarization) and axial $r$-direction (transverse to laser polarization), average resonance frequency $\omega_{\text{res}}(t)$ for the actual structure and charge state, number of emitted electrons $N_{\text{esc}}$ and dipole signal. From ref. [192], E. Suraud, and P. G. Reinhard, Phys. Rev. Lett. **85**, 2296 (2000), with permission from the American Physical Society @ 2000.

Fig. §26

Calculated harmonic spectrum for He at $\lambda = 616 \text{ nm}$ and intensity equal to $3.5 \times 10^{14}$ W/cm$^2$. The squares represent the experimental data [194], normalized to the value of the 33rd harmonic of the calculated spectrum. From ref. [195], C. A. Ullrich, S. Erhard and E. K. U. Gross, in *Super Intense

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Laser Atom Physics (SLAP IV), edited by H. G. Muller and M. A. Fedorov (Kluwer, Amsterdam, 1996), with permission from Kluwer @ 1996.
Figures

Fig. §1:
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Fig. §.19
Fig. §.20
Fig. §.21
Fig. §.22
Fig. §.23
Fig. §25

\begin{align*}
\omega_{\text{laser}} &= 2.9 \text{ eV} \\
I &= 9 \times 10^9 \text{ W/cm}^2 \\
T_{\text{pulse}} &= 240 \text{ fs}
\end{align*}

Na$_{41}^+$

- $\sqrt{\langle Z^2 \rangle}$
- $\sqrt{\langle r^2 \rangle}$

$\omega_{\text{res}}$ [eV]

$N_{\text{esc}}$

dipole

time [fs]
Fig. §.26
### Tables

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Table 6
Tables Captions

Table 1. Calculated RPA mean energies $e_1$ and $e_3$ (in eV) of the dipole surface collective mode of some neutral and charged sodium and potassium clusters. LDA and NL refer to the local density (LDA) and non-local (NL) approximations to exchange and correlation effects. The experimental surface plasma resonance energies are given in parenthesis. Data collected from ref. [15].

Table 2. The lowest $^1S \rightarrow ^1P$ excitation energies for alkaline-earth atoms and atoms of the Zn group. The experimental values (first column) [45] are compared with results calculated from equation (56) and (57) within LDA and OEP, and with ordinary $\Delta_{SCF}$ values (fourth column). The corresponding Kohn-Sham orbital energy differences $\Delta\epsilon$ are shown in the last two columns. All energies are given in eV.

Table 3. Comparison between the experimental singlet and triplet excitation energies for atoms and excitation energies calculated by the TDLDA, OEP and $\Delta_{SCF}$ methods [39]. The values of the experimental triplet transitions are the average over different spin-orbit components. All energies are given in eV.

Table 4. Calculated surface dipole plasmon energies (in eV) for the triaxial ground state of Na$_{12}$ and for the oblate (OE) and prolate (PE) isomers of Na$_{14}$, obtained from the RPA sum rule of eq. (71) [66].
Table 5. Energies, in eV, and strengths (between parentheses) of selected peaks in the optical response of the C$_{20}$ isomers of Figure 15 [162].

Table 6. Calculated quasiparticle energies of Na$_{20}$ in the spherical jellium model [33] compared with Kohn-Sham LDA [33] and WDA [32] energy eigenvalues.