The APMO-MOLPRO interface: Highly correlated electronic structure calculations with the inclusion of quantum nuclear effects at Hartree-Fock level
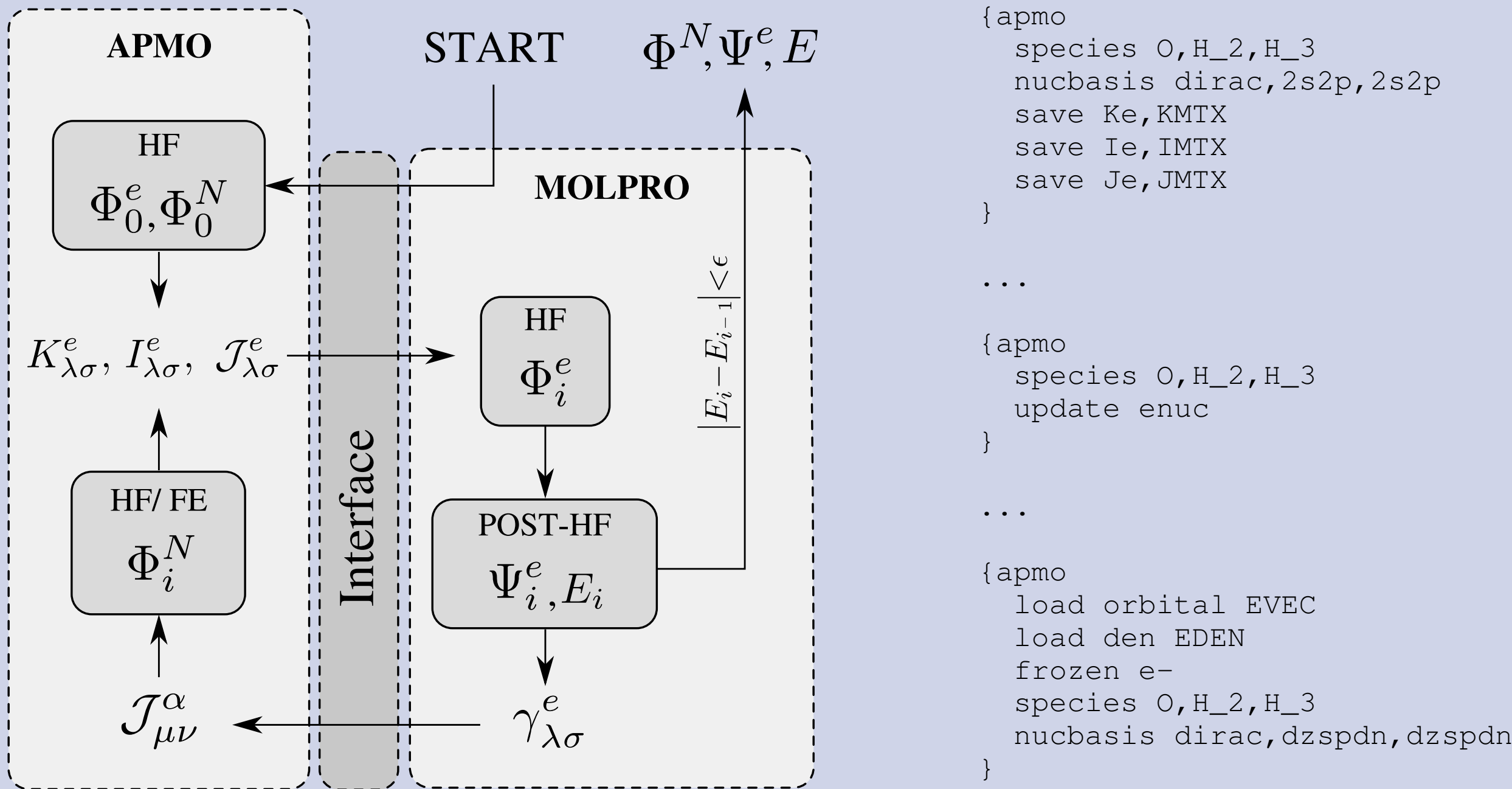
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Introduction

A computational interface between the MOLPRO [1] electronic structure package and the AMPO [2] code is presented here. The AMPO code is an implementation of the nuclear and molecular orbital approach [3,4,5] in which electrons and light nuclei of molecular systems are described simultaneously with molecular orbitals at Hartree-Fock and second-order Möller-Pleset levels of theory. The APMO-MOLPRO interface extends the applicability of the APMO code by allowing to correlate the electronic structure part at higher levels of ab-initio theory and to describe the nuclear response to electronic correlation effects. Some applications are presented to illustrate the advantages of this approach over standard electronic structure treatments.

Implementation


```
{apmo
   species O,H_2,H_3
   nucbasis dirac,2s2p,2s2p
   save Ke,KMTX
   save Ie,IMTX
   save Je,JMTX
}

...

{apmo
   species O,H_2,H_3
   update enuc
}

...

{apmo
   load orbital EVEC
   load den EDEN
   frozen e-
   species O,H_2,H_3
   nucbasis dirac,dzspdn,dzspdn
}
```

The interface APMO-MOLPRO has been fully implemented into the MOLPRO package version 2009.1. It is neccesary to have installed the APMO package (binary version available in [2]), make a few changes to the source code into the original code of MOLPRO, include the source file of the interface (apmo.f) and recompile the main MOLPRO executable. All parameters to control the calculation are selected directly from the MOLPRO input file.

Applications

Diatomic molecule of $^4He_2$

The biggest basis-set that have been used in a calculation of the ground-state of the X-dimer at FCI level is d-aug-cc-pV6Z (349 functions)[6], which lets to obtain a bound-state with only 19% of error respect to the exact value obtained from the empirical model Azis-Slaman (e=-0.000917cm-1). When the aug-cc-pVQZ (110 functions) at CCSD(T) is used, the potential energy curve provide unbound solutions, but including nuclear quantum effects through APMOLPRO the bound-state is recovered. In the figure can be seen details around of the minimum, where the differences among these methods are significant. This result appears to show that this method is in a similar way as well-known non-adiabatic corrections.
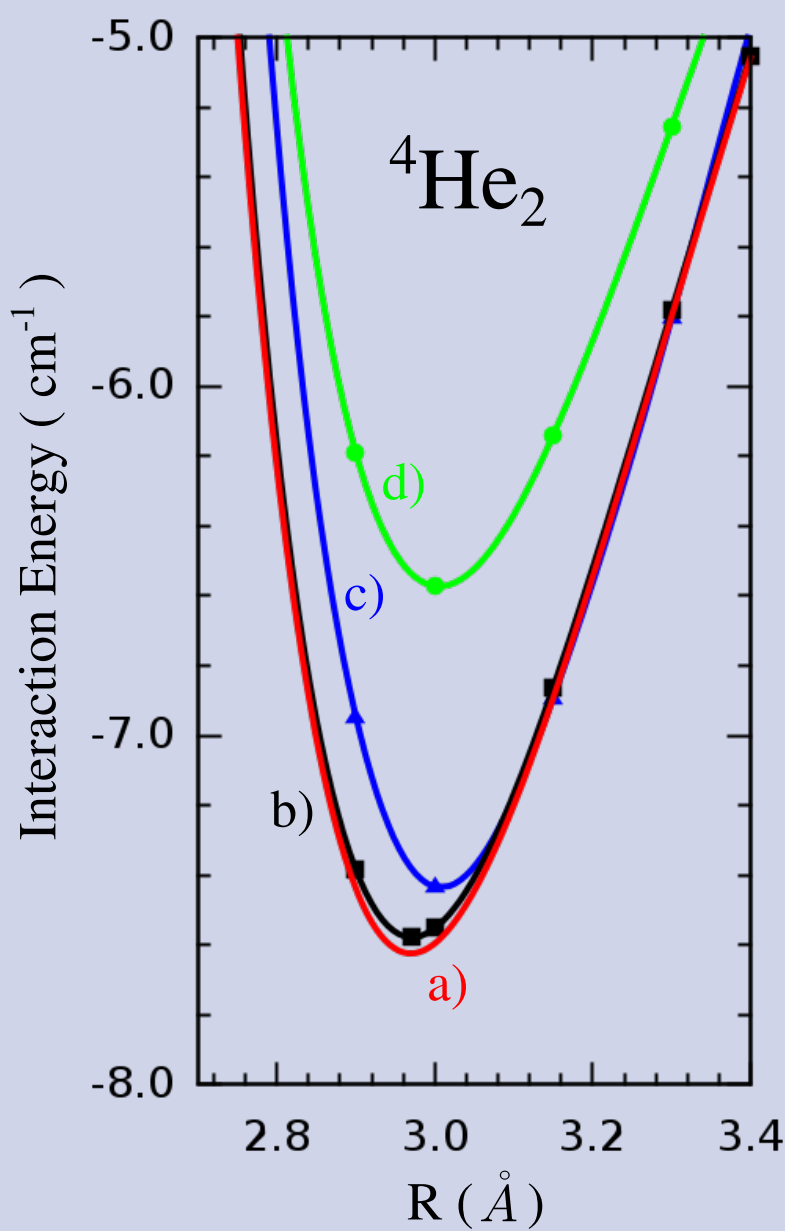
a) Empirical Azis-Slaman, b) FCI, d-aug-cc-pV6Z
c) APMOLPRO CCSD(T):CCSD, aug-cc-pVQZ:2s2p
d) CCSD(T), aug-cc-pVQZ

Model Systems for isotopic substitutions

Our objective, is not perform a quantitative study but rather to use these systems as models for the illustration of capabilities that the APMOLPRO interface can be offer. In this systems, only the the hydrogen nucleus is treated quantum mechanically. The convergence accuracy for the total energies was set to 10^{-8} a.u. and 10^{-5} for the gradient in optimization for geometries and centers of the nuclear bases.

The He,H$^+$ complexes were chosen as models because they have few enough electrons to be treated at FCI level and they are interesting as weakly-bound systems models. At HF level the behavior of its internuclear distance in both systems is H*<T<D<H, however, when the electronic correlation is included this behavior is kept in HeHHe$^+$ but is anomalous in HeH$^+$, which is the same at CCSD(T):CCSD (not shown here).

In the case of LiX (X=H,D,T) the bond distance is increased with the inclusion of the quantum hydrogens and even more when the electronic correlation is consider however, for the HF molecule, the behavior is inverted when the electronic correlation is taken in account. Normally this behavior has been understood in terms of the anharmonicity of the potential (T<D<H), but this result shows that probably the origin of this effect is a bit more complicated.

Conclusions

We applied the APMOLPRO interface program to analyze the nuclear quantum effects on the geometry for some prototype systems, it is shown that this extension of APMO although includes the nuclear-electron correlation only through the first-order density matrix instead of direct mode, it appears that this description is reliable, however it is necessary to study further systems in order to know its scope and limitations. The objective have been reached, now APMO can be use all available methods provided by MOLPRO at least for the electronic part.

Theory

In conventional calculations of electronic molecular structure based on the Born-Oppenheimer approximation (BO), the Hartree-Fock (HF) equations and its associated total energy in a basis of atomic orbitals, can be written as,

$$\mathbf{FC} = \mathbf{SC}\epsilon$$

$$E_{HF}^{BO} = tr\left[\mathbf{P}\left(\mathbf{K} + \mathbf{I} + \mathbf{G}(\mathbf{P})\right)\right] + \sum_{I,J \in \mathcal{N}} \frac{Z_I Z_J}{r_{I,J}}$$

where $\mathbf{P}$ is the matrix density (DM), $\mathbf{K}$ the kinetic-energy matrix, $\mathbf{I}$ represents the electron-nucleous interaction matrix and $\mathbf{G}$ the electron-electron interaction matrix.

When the electrons and some nuclei are represented as quantum particles (set $\mathcal{Q}$) treated at the same level, the HF equations and its associated total energy are modified as follows,

$$\mathbf{F}^\alpha \mathbf{C}^\alpha = \mathbf{S}^\alpha \mathbf{C}^\alpha \epsilon^\alpha, \quad \alpha \in \mathcal{Q}$$

$$E_{HF} = tr\left[\mathbf{P}^e\left(\mathbf{K}^e + \mathbf{I}^e + \mathcal{J}^e(\{\mathbf{P}^\alpha : \alpha \neq e\}) + \mathbf{G}^e(\mathbf{P}^e)\right)\right] + \sum_{\alpha \neq e} tr\left[\mathbf{P}^\alpha \mathbf{F}^\alpha\right] + \sum_{\gamma,\rho \in \mathcal{C}} \frac{Z_\gamma Z_\rho}{r_{\gamma,\rho}}$$

where appears a new term $\mathcal{J}^\alpha$, which lets to couple the HF equations among different quantum particles through the matrix densities $\mathbf{P}$ from the rest of the particles

$$\mathcal{J}_{\mu\nu}^\alpha(\{\mathbf{P}^\beta : \beta \neq \alpha\}) = \sum_{\beta \neq \alpha} \sum_{\lambda,\sigma=1}^{N_{bf}^\beta} P_{\lambda\sigma}^\beta (\phi_\mu^\alpha \phi_\nu^\alpha \,|\, \phi_\lambda^\beta \phi_\sigma^\beta)$$

It is possible to show that making the following substitutions, the electronic HF equations and its total energy in both schemes are equivalent

$$\mathbf{K} \Longleftarrow \mathbf{K}^e$$

$$\mathbf{I} \Longleftarrow \mathbf{I}^e + \mathcal{J}^e(\{\mathbf{P}^\alpha : \alpha \neq e\})$$

$$\sum_{I,J \in \mathcal{N}} \frac{Z_I Z_J}{r_{I,J}} \Longleftarrow \sum_{\alpha \neq e} tr\left[\mathbf{P}^\alpha \mathbf{F}^\alpha\right] + \sum_{\gamma,\rho \in \mathcal{C}} \frac{Z_\gamma Z_\rho}{r_{\gamma,\rho}}$$

so, following this technique, we were able to deceive to the MOLPRO program in order to include the interaction of the electron with the quantum nuclei at HF level.

Aiming to describe the electrons at high correlation level using the available methods in MOLPRO, for example Full-CI, Coupled-Cluster, among others, we have modified the inter-particle interaction matrices $\mathcal{J}^\alpha, \alpha \neq e$, replacing the DM $\mathbf{P}^e$, for the First-Order Reduced Density Matrix γ^e. It is important to point out, that both matrices coincides if only one configuration is considered.

$$\mathcal{J}^\alpha(\gamma^e, \{\mathbf{P}^{\alpha'} : \alpha' \neq \alpha, e\}) \Longleftarrow \mathcal{J}^\alpha(\mathbf{P}^e, \{\mathbf{P}^{\alpha'} : \alpha' \neq \alpha, e\})$$

This is equivalent to represent the total wave function in the Configuration-Interaction (CI) scheme as ($\mathbf{r}^N = \{\mathbf{r}^\alpha : \alpha \neq e\}$)

$$\Psi\left(\mathbf{r}^e, \mathbf{r}^N\right) \approx \Phi_0^N(\mathbf{r}^N) \sum_I C_I \Phi_I^e(\mathbf{r}^e) \qquad \Phi_I^N(\mathbf{r}^N) = \prod_{\alpha \neq e} \Phi_I^\alpha(\mathbf{r}^\alpha)$$

where the elements of the reduced density matrix takes the following form

$$\gamma_{ij}^e = \sum_{IJ} C_I C_J \langle \Phi_I^e | \hat{E}_{ij} | \Phi_J^e \rangle$$

It is important to take into account, that the complete Full-CI wave function for all quantum particles is

$$\Psi\left(\mathbf{r}^e, \mathbf{r}^N\right) = \sum_I \sum_{I'} C_{II'} \Phi_I^e(\mathbf{r}^e) \Phi_{I'}^N(\mathbf{r}^N)$$

	APMO	APMOLPRO
Molecule	$R_e(\text{Å})$	$R_e(\text{Å})$
	HF	FCI:FCI
HeH$^+$	0.7946	0.7631
HeD$^+$	0.7871	0.7640
HeT$^+$	0.7840	0.7626
HeH*	0.7705	0.7748
	HF	CCSD(T):CCSD
HeHHe$^+$	0.9464	0.9610
HeDHe$^+$	0.9403	0.9500
HeTHe$^+$	0.9376	0.9453
HeHHe*	0.9257	0.9249

Elec. basis set: aug-cc-pVQZ
Nuc. basis set: DZSPD
* Conventional electronic calculation

	APMO		APMOLPRO	
Molecule	$R_e(\text{Å})$	$\mu(D)$	$R_e(\text{Å})$	$\mu(D)$
	HF		FCI:FCI	
LiH	1.6275	0.60288	1.6549	0.5889
LiD	1.6213	0.60290	1.6448	0.5898
LiT	1.6186	0.60294	1.6415	0.5902
LiH*	1.6069	0.60272	1.6098	0.5893
	HF		CCSD(T):CCSD	
HF	0.9044	0.19389	0.8755	0.1697
DF	0.9024	0.19215	0.8781	0.1709
TF	0.9015	0.19138	0.8798	0.1716
HF*	0.8972	0.18819	0.9128	0.1810

Elec. basis set: LiH, aug-cc-pVTZ. HF, aug-cc-pVQZ
Nuc. basis set: DZSPD
* Conventional electronic calculation

References

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