Vibrational transition rule during a through-bond electron transfer process

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Abstract

The transition rule governing the inelastic excitations of molecular vibrations occurring during a molecular through-state electron transfer process is presented. Using an effective Hamiltonian model, it is shown that the quantum time oscillation of the intermediate electronic state population triggers this transition. Its corresponding quantum oscillation frequency has to be equal to a quantum of vibration. This transition rule is extended to the full spectrum of a quantum vibrator. This new transition rule is expected to be robust when electronically coupling the molecule to the metallic pads of a voltage-biased tunnel junction.

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1. Introduction

Under a finite bias voltage, the tunnel current passing through a metal-molecule-metal junction is the result of billions of electron transfer events per second occurring through the low lying electronic states of the molecule [1, 2]. A macroscopic ammeter positioned along the external circuit measures the corresponding current intensity that is the average number of electrons passing through the junction per second. Many interesting time dependent events occurring inside the junction during a given electron transfer event through the molecule still show up after this time averaging [3]. One is the quantum interference showing up when there are for example two different and independent electron transfer pathways through the molecule (topological or relative to states like in [4, 5]) resulting in time dependent destructive interferences per electron transfer event. As a result, the tunnelling current can be much lower than in the case of a molecule with two identical branches. Inelastic phenomena also show up in the tunnel current by a small intensity change when an inelastic tunnel channel is reached [6]. This is usually interpreted using a standard energy conservation argument i.e. a molecular vibration transition occurs when the bias voltage applied to the junction equals a quantum of vibration of the molecule vibrational manifold. This defines a transition rule from the ground to some vibronic excited state of the molecule which can be traced back to the standard problem in quantum physics of an electromagnetic plane wave interacting with a two-state quantum system originally prepared in its ground state [7]. In the case of a through-molecule electron transfer event of interest here, no plane wave is involved. Each time dependent electron transfer event results from the
preparation by the tunnel junction of an initial electronic wave packet on
one electrode, propagating through the molecule, reaching the second elec-
trode and followed by the decoherence of the wave packet on this second
electrode [1]. When voltage biased, the same time sequence is randomly and
seldom reproduced by the tunnel junction leading to a net current intensity.

In this letter, we show how a through-state electron transfer event induces
a vibrational transition following a transition rule different from the usual one
mentioned above. For an inelastic transition to occur in the through-state
tunneling regime, the difference in energy between the two vibrational eigen-
states has to be equal to the oscillation frequency of the population of the
intermediate electronic state supporting the vibrational manifold. Actually,
it is demonstrated in the following that this oscillation plays the role of the
oscillating electromagnetic field in the standard transition-like model where
a two-state quantum system interacts with this electromagnetic field [8]. Our
new transition rule can be considered as a generalization of the Rabi formula
to intramolecular resonant and non-resonant transitions.

To demonstrate this new transition rule, a three-electronic state system is
used. The system is prepared in a non-stationary initial state |1⟩, simulating
the preparation an elementary electron transfer event by the tunnel junction.
Then, the |Ψ(t)⟩ time dependent wave packet issued from |1⟩ reaches almost
periodically in time its symmetric target state |3⟩ through an electronic inter-
mediate state |2⟩, whose energy is harmonic as a function of a given mechani-
cal degree of freedom. This model system and its Hamiltonian are introduced
in section 2 together with its exact time dependent evolution starting from
|1⟩. With the help of perturbation theory, the new transition rule is demon-
strated in section 3, and we provide an effective two-state vibrational system to explain this new transition rule. In section 4, this rule is generalized to a series of transitions occurring through the complete vibrational spectrum of the intermediate electronic state. Finally, some consequences of this new transition rule are discussed in section 5.

2. The through-state transition rule

To demonstrate how a non-resonant through-state electron transfer process can trigger a vibrational transition, a three-state symmetric electronic quantum system is constructed where an initial non-stationary state $|1\rangle$ is prepared. The population of this state evolves almost periodically in time toward the target state $|3\rangle$ [9]. The intermediate state $|2\rangle$ is coupled electronically and symmetrically to $|1\rangle$ and $|3\rangle$ and there is no direct (through space) coupling between $|1\rangle$ and $|3\rangle$. State $|2\rangle$ is the ground state of a vibrational manifold described by the set of vibrational states $\{|n\rangle\}$. For simplicity, only $|n = 0\rangle$ and $|n = 1\rangle$ will be considered in this section. They form the ground and first vibrational excited states where a transition from $|n = 0\rangle$ to $|n = 1\rangle$ is triggered by the through-$|2\rangle$ electron transfer process. In this simple example, the Hilbert space is generated by the tensor product $|i\rangle \otimes |n\rangle$ where $i = 1, 2, 3$ for the three electronic states described above and $n = 0, 1$ for the two vibrational states. In the figure 1, the horizontal lines represent the $|i, n\rangle$ states. For example, the three upper states are $|1, 1\rangle$, $|2, 1\rangle$ and $|3, 1\rangle$, from left to right. They correspond to the states necessary for describing the electron transfer through the vibrationally excited state. The control parameters of this inelastic electron transfer phenomenon are the vibrational
coupling $\alpha$, the electronic coupling $q$, the frequency of the quantum vibrator $\Delta \omega$ and the central electronic state energy shift $e$. The off-diagonal matrix element $q$ is responsible for the electronic coupling between $|1\rangle$ and $|2\rangle$ and between $|2\rangle$ and $|3\rangle$. Given a quantum system prepared in $|1\rangle$ (for triggering the through state $|2\rangle$ electron transfer process) and reaching its symmetric state $|3\rangle$, a unique coupling $q$ is defined between these two states and $|2\rangle$.

The time dependent quantum state $|\Psi(t)\rangle$ describing the time evolution of this six-state system can be decomposed on the $|i,n\rangle$ basis set leading to $|\Psi(t)\rangle = \sum_{i,n} C_{i}^{n}(t)|i,n\rangle$ and the Hamiltonian generating this evolution can be written on the same basis set:

$$
\mathcal{H} = \begin{pmatrix}
0 & q & 0 & 0 & 0 & 0 \\
q & e & q & 0 & \alpha & 0 \\
0 & q & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \Delta \omega & q & 0 \\
0 & \alpha & 0 & q & e + \Delta \omega & q \\
0 & 0 & 0 & q & \Delta \omega & 0
\end{pmatrix}.
$$

(1)

The initial non-stationary state being $|1,0\rangle$, the time-dependent Schrödinger equation was solved using a standard split-operator algorithm, calculating at each time-step the quantity $| \langle 3,1 | e^{-i\mathcal{H}t} | 1,0 \rangle |^2$. It gives the probability to excite the vibrational system once an electron has been transferred between $|1,0\rangle$ and $|3,1\rangle$ through $|2,0\rangle$. For a fixed value of $\alpha$ and $q$, the maximum of this probability over time is simply:

$$
P_{1}(\Delta \omega, e) = \max_{t} | \langle 3,1 | e^{-i\mathcal{H}t} | 1,0 \rangle |^2.
$$

(2)
This quantity is defined to track the rule that governs the transition \( i.e. \) the maximum population that has actually been transferred regardless of the time dependent behavior of the target state population.

As shown by the contour plot in figure 2 (a), resonant features are observed for this transition probability maxima. For quasi-degenerate vibrational cases \( i.e. \) for extremely low \( \Delta \omega \) values, \( P_1 \) reaches its 0.25 maximum value. More interestingly, in a non-degenerate case and for a fixed \( q \) value, if \( e \) is ramped up (to increase \( \sqrt{e^2 + 8q^2} \)), another maximum in \( P_1 \) can be observed on the figure 2 (a) contour plot corresponding to the new resonance condition:

\[
\Delta \omega = \sqrt{e^2 + 8q^2}. \tag{3}
\]

Therefore, to obtain a maximum population transfer form \( |n = 0\rangle \) to \( |n = 1\rangle \) during a through-state electron transfer process, \( \sqrt{e^2 + 8q^2} \) has to be tuned relative to \( \Delta \omega \). This is a new transition rule which notably differs from the standard one [6]: \( \Delta \omega = \Delta e \). This simple \( \Delta \omega = \Delta e \) rule comes from the time evolution of a two-state system (say \( |a\rangle \) and \( |b\rangle \)) instead of a three-state quantum system. It can be demonstrated by preparing this two-state system in the initial state \( |a\rangle \) coupled to a target state \( |b\rangle \) with \( \Delta e \) the energy difference between the two. As supposed in [6], when the vibrator is only coupled to \( |b\rangle \), the \( \Delta \omega = \Delta e \) transition rule results from the maximization of the population of the \( |b, n = 1\rangle \) target vibronic state.

Our new transition rule \( \Delta \omega = \sqrt{e^2 + 8q^2} \) is a generalization of this result showing that even in a non-resonant electron transfer process, an inelastic transition can occur. For a small value of \( q \), this new rule introduces a small
energy shift to \( e \). For a large \( q \) (or a large \( e \)), an inelastic transition can only occur for large \( \Delta \omega \) which corresponds necessarily to higher vibrational states of the central vibrator. This requires a generalization of (3) to a larger vibrational manifold (see section 4) as presented in the next section. Notice also that the new resonance line on the 2 (a) resonance contour plot dies off for large \( \sqrt{e^2 + 8q^2} \) values indicating also the presence of an envelop term controlling the Lorentzian shape of this inelastic transition as discussed in the next section.

3. Numerical and analytical analysis of the new through-state transition rule

The new resonance line observed on figure 2 (a) contour plot can be obtained using a simple perturbative expansion since \( \alpha \) is usually small as compared to \( q \). When decomposing (1) in \( \mathcal{H} = H + W \) with \( H \) the unperturbed Hamiltonian and \( W \) the perturbation, \( W \) is a sparse matrix that contains only the vibrational coupling elements \( \alpha \). Given its block-diagonal structure, \( H \) can now be analytically diagonalized. Its eigenvalues \( \varepsilon_n \) are given by:

\[
\begin{align*}
\varepsilon_1 &= \frac{e + \sqrt{e^2 + 8q^2}}{2} \\
\varepsilon_2 &= 0 \\
\varepsilon_3 &= \frac{e - \sqrt{e^2 + 8q^2}}{2} \\
\varepsilon_4 &= \varepsilon_1 + \Delta \omega \\
\varepsilon_5 &= \varepsilon_2 + \Delta \omega
\end{align*}
\]
\[ \varepsilon_6 = \varepsilon_3 + \Delta \omega. \] (9)

In this case, the perturbed eigenstates are given to the first order by:

\[ |\tilde{\xi}_1 \rangle = |\xi_1 \rangle + \frac{\alpha}{\Delta \omega} a_1^1 |\xi_4 \rangle + \frac{\alpha}{\sqrt{\varepsilon^2 + 8q^2 - \Delta \omega}} a_6^1 |\xi_6 \rangle \] (10)

\[ |\tilde{\xi}_2 \rangle = |\xi_2 \rangle \] (11)

\[ |\tilde{\xi}_3 \rangle = |\xi_3 \rangle + \frac{\alpha}{\sqrt{\varepsilon^2 + 8q^2 + \Delta \omega}} a_4^3 |\xi_4 \rangle + \frac{\alpha}{\Delta \omega} a_6^3 |\xi_6 \rangle \] (12)

\[ |\tilde{\xi}_4 \rangle = |\xi_4 \rangle + \frac{\alpha}{\Delta \omega} a_1^1 |\xi_1 \rangle + \frac{\alpha}{\sqrt{\varepsilon^2 + 8q^2 + \Delta \omega}} a_3^1 |\xi_3 \rangle \] (13)

\[ |\tilde{\xi}_5 \rangle = |\xi_5 \rangle \] (14)

\[ |\tilde{\xi}_6 \rangle = |\xi_6 \rangle + \frac{\alpha}{\sqrt{\varepsilon^2 + 8q^2 - \Delta \omega}} a_1^6 |\xi_1 \rangle + \frac{\alpha}{\Delta \omega} a_3^6 |\xi_3 \rangle, \] (15)

the \(|\xi_n \rangle\) being the eigenstates of the unperturbed Hamiltonian \(H\).

To the first order, only the states \(|\tilde{\xi}_{q=1,3,4,6} \rangle\) are ‘mixtures’ of other states and the perturbation does not cause any changes upon states \(|\xi_{q=2,5} \rangle\). Each \(|\tilde{\xi}_q \rangle\) belonging to one vibrational state can be written as a combination of states belonging to the other vibrational state. For example in (10), the unperturbed state \(|\xi_1 \rangle\) belonging to \(n = 0\) is mixed up with \(|\xi_4 \rangle\) and \(|\xi_6 \rangle\), both belonging to \(n = 1\).

The coefficients \(a_q^g\) are related to the projections of unperturbed \(|\tilde{\xi}_q \rangle\) states on canonical \(|i, n\rangle\) states. We have explicitly left the prefactor \(\alpha\) in each term as well as in the denominator \(1/(\varepsilon_q - \varepsilon_p)\), because it explains the behavior of the resonance maximum displayed in figure 2 (a). Actually, finding \(\Delta \omega\) as a denominator in (10), (12), (13) and (15), indicates that there is a strengthening of the coupling between states belonging to different vibrational states when \(\Delta \omega\) vanishes. This explains the maxima in the transition probability.
in the quasi-degenerate case mentioned above. Similarly, the denominators of the form $\sqrt{e^2 + 8q^2} - \Delta \omega$ appearing in (10) and (15), confirm the validity of the transition rule (3), that describes the transition from $|n = 0\rangle$ to $|n = 1\rangle$. Notice also that the denominator $\sqrt{e^2 + 8q^2} + \Delta \omega$ in (12) and (13) can be interpreted as an anti-resonance. This is reminiscent of a two-state quantum system coupled via an oscillating field [8]. In the rotating wave approximation, the anti-resonant term is neglected, keeping only the resonant contribution in order to define a transition rule [7].

It is not surprising that $\sqrt{e^2 + 8q^2}$ controls the through-state inelastic transition since according to [9] and for a simple three-state system with no vibronic structure on $|i = 2\rangle$, the $|i = 2\rangle$ population $p(t)$ is found to oscillate in time following the analytical expression:

$$p(t) = \frac{4q^2}{e^2 + 8q^2} \sin^2 \left( \frac{\sqrt{e^2 + 8q^2} t}{2} \right),$$

when the initial state is prepared in $|i = 1\rangle$.

Therefore, a simple model leading to (3) can be constructed using a two-state $|n = 0\rangle$ and $|n = 1\rangle$ quantum system. In this model, the time oscillating term in (16) becomes an effective time-dependent external field $\cos(\sqrt{e^2 + 8q^2} t)$ that triggers the transition from $|n = 0\rangle$ to $|n = 1\rangle$. In constructing such a model, the full six-dimensional Hilbert space shown in figure 1 must be reduced to two dimensions. To exactly obtain this reduction of dimension, the partial trace of the density operator $\hat{\rho}(t) = |\Psi(t)\rangle \langle \Psi(t)|$ has to be taken over the electronic states leading to the reduced $\hat{d}(t) = Tr_e[\hat{\rho}(t)]$ density matrix. Then, a time evolution equation has to be constructed for $\hat{d}(t)$. Here, it is not possible to get a standard pure $\hat{d}(t)$ like in the standard
\[ \frac{d}{dt} \hat{d}(t) = [H_{Rabi}, \hat{d}(t)] \] evolution equation since the detailed calculations lead to an infinite series of entangled Liouvillian-like superoperators [10]. Therefore, we have preferred to build up an effective \( H_{Rabi} \) Hamiltonian starting from the oscillation in (16) and adjusting the normalization of \( \hat{d}(t) \) with respect to the trace \( Tr_{e,v}(\hat{\rho}(t)) = 1 \) overall normalization condition. Following this procedure, the resonance map found in figure 2 (a) for \( \Delta \omega \neq 0 \) can be recovered using the effective Rabi-like Hamiltonian:

\[
H_{Rabi} = \begin{pmatrix}
\Delta \omega & \alpha \cos(\tilde{\omega}t) \\
\alpha \cos(\tilde{\omega}t) & 0
\end{pmatrix}
\] (17)

expressed here on the \( \{|n = 0\rangle, |n = 1\rangle\} \) vibrational basis set with \( \tilde{\omega} = \sqrt{e^2 + 8q^2} \).

Using (17), the time-dependent Schrödinger equation can be solved analytically in the rotating wave approximation to calculate the probability \( |D_1(t)|^2 = \langle 1|\hat{d}(t)|1 \rangle \) to reach \( |n = 1\rangle \) starting at time \( t = 0 \) in the \( |n = 0\rangle \) ground vibrational state:

\[
|D_1(t)|^2 = A \frac{4q^2}{e^2 + 8q^2} \frac{\alpha^2}{(\tilde{\omega} - \Delta \omega)^2 + \alpha^2} \sin^2(\Omega_{Rabi} t),
\] (18)

where \( \Omega_{Rabi} = \frac{1}{2} \sqrt{(\tilde{\omega} - \Delta \omega)^2 + \alpha^2} \). Notice that this analytical solution was obtained by imposing the normalization condition \( |D_0(t)|^2 + |D_1(t)|^2 = A \frac{4q^2}{e^2 + 8q^2} \). According to (16), the maximum possible population for \( |D_0(t)|^2 = \langle 0|\hat{d}(t)|0 \rangle \) is \( \frac{4q^2}{e^2 + 8q^2} \). But it is also necessary to take into account the Hilbert space size reduction where some population is still on the four dimensions not considered in our simple model leading to \( |D_0(t)|^2 + |D_1(t)|^2 < \frac{4q^2}{e^2 + 8q^2} \). This explains the \( A \) factor in (18).
Finally, the maximum value of $|D_1(t)|^2$ follows a Lorentzian behavior giving the variation of transition probability from $|n = 0\rangle$ to $|n = 1\rangle$ induced by the effective oscillating field of amplitude $\alpha$ introduced in $H_{Rabi}$. The Lorentzian maximum is obtained when $\tilde{\omega} = \sqrt{e^2 + 8q^2} = \Delta \omega$. This is exactly the new transition rule obtained in (3). The corresponding transition map is given in figure 2 (b) and has to be compared to figure 2 (a). The set of maxima across the plot are nicely reproduced. However, the features appearing at small $\Delta \omega$ in figure 2 (b) do not appear in figure 2 (a) because our transition rule does apply to them since at low $\Delta \omega$ ($\Delta \omega < \alpha$) the rotating wave approximation is expected to fail.

During a through-state electron transfer process, the evolution of the population of this intermediate state plays the role of an effective perturbing oscillating field. It triggers a transition from the ground to the excited state of a quantum vibrator interacting with this intermediate electronic state. Before discussing the consequence of this results, its generalization to a quantum vibrator characterized by its full quantum spectrum is proposed in the following.

4. **Generalization of the through-state transition rule to many vibrational states**

The generalization of the through-state transition rule (3) is obtained by keeping the electronic subspace unchanged and by extending the vibrational subspace to an arbitrary number of states ($n > 1$). Similarly to the model represented in figure 1, the central state is the only one to be coupled to a vibration and the value of $\alpha$ is still the same as previously, regardless of
the vibrational state considered. They are only coupled to the first neighbor states because the vibrator is supposed here to be harmonic. Note however that the actual couplings are different from vibrational state to vibrational state because of the normalization properties of the ladder operators of a quantum harmonic oscillator. In general, the vibrational off-diagonal coupling elements are given by $\langle 2, n|H|2, n + 1 \rangle = \alpha \sqrt{n + 1}$.

To explore the time dependent evolution of the vibronic state population, the same approach as described above was followed, tracking over time the probability maxima. Let us define the following quantity:

$$P_N(\Delta \omega, e) = \max \sum_{n=1}^{N} | \langle 3, n|e^{-iHt}|1, 0 \rangle |^2, \quad (19)$$

$P_N$ gives the maximum transition probability for all vibrational states. In general, for a complete space, the sum should go up to infinity. But for numerical reasons, it was truncated to a finite value $N$.

In the figure 3, the panels (a), (b) and (c) present $\max \sum_{n=1}^{N} | \langle 3, n|e^{-iHt}|1, 0 \rangle |^2$ for $n = 1, 2, 3$ respectively. Qualitatively, the plots show the same features than the one observed in figure 2 (a). In particular, the linear behavior of the maxima is found again in the regimes where $\Delta \omega$ is close to zero and in the non-degenerate regime. Quantitatively however, in the latter case, the slopes along the resonant lines are $1, \frac{1}{2}$ and $\frac{1}{3}$ for plots (a), (b) and (c) respectively. In figure 3 (d), the full $P_N$ variations are represented where the three contributions now combined. Considering the behavior of the resonance contour plot of each set of maxima, the following condition has to be fulfilled for a vibronic transition to occur between states $|1, 0\rangle$ and $|3, n\rangle$:
\[
\Delta \omega = \frac{1}{n} \sqrt{e^2 + 8q^2}.
\]  

(20)

This is the generalization of the through-state inelastic transition rule (3). One advantage with (20) compared to (3) is that the division by \( n \) renders the resonance condition to be quite easily fulfilled at large \( e \) and \( q \) values.

5. Discussion

The new transition rule \( \Delta \omega = \frac{1}{n} \sqrt{e^2 + 8q^2} \) is a generalization of the standard inelastic transition rule \( \Delta \omega = \Delta e \) used by many authors [6] in the context of scanning tunnel microscope (STM) spectroscopy and of electronic transport through a single molecule. They both come from the theory of the time evolution of a quantum system made of two different degrees of freedom where one is initially in its ground state while the other starts the quantum time evolution. This demonstrates that even for molecular electronic states not well coupled to the electrodes of a tunneling junction, inelastic effects can show up.

These two transitions rules can be compared in the case of an STM tunnel junction. When the junction is biased with a voltage \( V \), the \( \Delta \omega = \Delta e \) transition rule leads to \( \Delta \omega = V \) meaning that, as discussed in [6] and used by a large number of authors afterwards, a vibrational transition occurs when the bias voltage reaches a vibration quantum assuming that the corresponding ground vibronic state is very close in energy to the electrode Fermi energy. With the new transition rules (3) and (20), when only one effective intermediate electronic state is involved, an inelastic transition will occur when \( \Delta \omega = \sqrt{(e - V)^2 + 8q^2} \) because the effect of a positive bias \( V \) is to lower the
energy of the intermediate state relative to the available electrode electronic states. This can be generalized to more than one electronic intermediate state. Notice also that when the bias voltage on a tunnel junction is ramped up to reach \( e.g. \) the first electronic excited state of a molecule embedded in this junction, a vibrational transition will occur for a \( V \) just below the resonance energy \( e \). This new transition rule deviates strongly from the previous one, especially for large values of the electronic coupling \( q \).

In this case, the vibration transition rule is certainly not the standard \( \Delta \omega = V \) transition rule because \( V \) is too large compared to \( \Delta \omega \). Our new transition rule is therefore very well adapted to the inelastic phenomena occurring for example when extracting an adsorbate from a surface or when triggering the rotation or the translation of a molecule on a surface. Interestingly, the generalization (20) also applies for the inelastic excitation of high energy vibration modes starting from the ground state of an adsorbate which electronic ground state is far deep in energy as compared to the metal electrode Fermi energy of the junction. This is for example the case in the STM Xenon switching phenomenon [11].

6. Summary and conclusions

In this work, we have demonstrated the general rule that governs the vibrational transition during a through-state electron transfer phenomenon. Using an effective model, we have shown how the time oscillation of the population of the central electronic state coupled to the vibrator triggers the transition and not some coincidence in energy: the corresponding oscillation frequency has to be equal to a quantum of vibration for an inelastic transition
to occur. This transition rule has been generalized for many vibrational states of this vibrator inelastically coupled to the central electronic state. This new inelastic transition rule is expected to be robust when electronically coupling this system to the metallic pads of a voltage-biased or a current-fed tunnel junction.

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References


Figure 1: Schematic representation of the model. The electronic subspace is displayed horizontally, and the vibrational subspace vertically. The parameters $\alpha$, $q$, $\Delta \omega$, and $\epsilon$ are the vibrational coupling, the electronic coupling, the vibrational quantum and an energy shift respectively.

Figure 2: (a) Maximum transition probability plot as a function of the vibrational quantum $\Delta \omega$ and the driving frequency $\sqrt{\epsilon^2 + 8q^2}$ at a fixed value of the electronic coupling $q = 10$ meV and for a range of values of $\epsilon$ spanning the interval $[0, 100]$ meV. The vibrational coupling was set to $\alpha = 5$ meV. The color box at the right of the plot gives the value of the probability. The higher values are obtained for the degenerate case $\Delta \omega = 0$, and another set of non zero values shows a linear behavior across the plot. (b) Maximum transition probability plot obtained with the effective Rabi-like model using (17). The parameters used are the same as in (a), $A$ has been set to 0.1.
Figure 3: Maximum transition probability plots as a function of the vibrational quantum $\Delta \omega$ and the driving frequency $\sqrt{e^2 + 8q^2}$ at a fixed value of the electronic coupling $q = 10$ meV and for a range of values of $e$ spanning the interval $[0, 100]$ meV. The vibrational coupling was set to $\alpha = 10$ meV. The number of vibrational states included in this calculation was 4 ($n \in [0, 3]$). The color box at the right of each plot gives the value of the probability. The plots (a), (b) and (c) show the results only for $n = 1, 2, 3$ vibrational states respectively. Plot (d) shows the result for all the vibrational contributions.