Electron−Nuclear Coupling in the Classical Limit for the Electronic Degrees of Freedom[†]

F. Remacle[‡] and R. D. Levine*[,§,||]

Département de Chimie, B6, Université de Liège, B 4000 Liège, Belgium, The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University, Jerusalem 91904, Israel, and Department of Chemistry and Biochemistry, University of California Los Angeles, Los Angeles, California 90095

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The use of a classical limit for the electronic degrees of freedom avoids the need to keep the nuclei clamped while solving for the dynamics of the electrons. The Hamiltonian for the electrons will then depend on the nuclear coordinates as dynamical variables. The resulting (classical) electron−nuclear coupled equations of motion exhibit dynamical symmetry and are shown to depend only on the ratio, κ^4, of the electron to nuclear mass. We explore the coupled electron−nuclear dynamics as a function of κ for the special case of a single electron moving between two centers. In the dynamical regime where the nuclei are heavy and the Born−Oppenheimer separation should work, the full dynamical procedure is in excellent agreement with the nuclear dynamics as computed using the Born−Oppenheimer separation. In the opposite regime where the period of the electronic motion is long, a case that can be physically realized for very high Rydberg states, one reaches an 'inverse' behavior where the nuclei adiabatically adjust to the slow electronic motion. The failure of the Born−Oppenheimer separation, as judged by the electronic coupling not being governed solely by the instantaneous position of the nuclei, is more severe when the initial electronic state is not stationary.

1. Introduction

The different time scales for electronic and nuclear motion are central to many notions in chemistry. The most important idea that emerges from this separation is arguably that of a geometrical structure of a molecule. This is defined as the minimum on the potential energy, which is determined by the fast moving electrons. It is becoming abundantly clear that the success of this idea is closely related to the ground electronic state being typically well-separated in energy from the excited states. Higher up in energy one finds a maze of conical intersections[1−3] that allows for a very facile coupling between electronic and nuclear motions. To describe this coupling one often begins with a Born−Huang expansion (see Appendixes VII and VIII in ref 4; see also ref 5) of the complete wave function as a sum of components, each one representing a separated nuclear and electronic motion. These component wave functions are then coupled by the so-called non Born−Oppenheimer coupling terms that arise from the dependence of the electronic wave functions on the nuclear coordinates. In the Born−Oppenheimer approximation, the electronic wave functions are taken to depend parametrically (and not dynamically) on the nuclear coordinates and so the coupling terms vanish. There are other methods (e.g., refs 6−8) that do not start from a Born−Huang[4] expansion. The procedure, to be discussed below, where we simultaneously solve for the motion of electrons and nuclei is similar in spirit to these alternative routes. There is one essential difference that is further discussed. The classical variables that we use for the electron are *not* its classical coordinates. Rather, these are coordinates that specify the occupancy of the possible site orbitals. Meyer and Miller have very effectively employed classical coordinates that specify occupancy of different electronic states.[9,10] Their method is sometimes known as the 'classical electron analogue' model.[11] By using coordinates for site orbitals we are able to discuss situations where many electronic configurations interact, which was our original motivation. In the present problem the site occupancy coordinates provide a direct view of the electron transfer between the sites, a transfer that goes on even when the system is in a (Born−Oppenheimer) stationary electronic state.

In this exploratory study we solve for the motion of one electron as it migrates between two centers while it is dynamically coupled to the classical relative motion of the two nuclei. Our intention is to span the range of possible behavior, from where the nuclei move slowly and the electron adiabatically follows the motion of the nuclei to the opposite extreme (the so-called inverse Born−Oppenheimer approximation[12]) where it is the slow electron that moves in the effective potential determined by the faster moving nuclei.

The model here developed is for the purpose of examining the motion of the electron due to the presence of the other center, a coupling that is modulated by the vibrating nuclei. There is a class of models in electron-transfer theory, known sometimes as 'the spin boson Hamiltonian'.[13] We emphasize that there is an essential physical difference between our system and the problem addressed by such models. For us, in the Born−Oppenheimer limit, the nuclei vibrate within the potential determined by the migrating electron. In models for electron transfer the vibrational coordinate is not necessarily the intersite separation. It can be a solvent coordinate or an intramolecular vibration, but it is not the coordinate we have in mind here. The difference is in the back-coupling. In both sets of models the vibration can perturb the electronic motion. Here however there is a dynamic feedback because the motion of the electron determines the potential for the vibration of the nuclei.

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* Corresponding author. Fax: 972-2-6513742. E-mail: rafi@fh.huji.ac.il.

[‡] Université de Liège.

[§] The Hebrew University.

[||] University of California Los Angeles.

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There is a critical approximation in our method, and this is the use of classical mechanics to describe the motion of the nuclei. In this respect, the closest to what we do is probably the dynamical Feynman theorem of Kerner.[14] The use of a classical limit for the electronic motion is here not an approximation because we use a classical limit[15] that, in the orbital approximation, is exactly equivalent to quantum mechanics.[16] The way of taking the classical limit for the electronic degrees of freedom is not the same as in the method used by Meyer and Miller[9,10] and its semiclassical extensions.[11] But the way we take the limit leads to intermediate results closely related to those provided by a method proposed by White and Miller.[17] The way we take the classical limit expresses the Hamiltonian in terms of the occupancy of the different site orbitals. For this reason it is necessary to note that the limit is consistent with the Pauli principle.

The quantum chemical procedure of configuration interaction offers a suitable framework for the comparison of what we do with the method of Meyer and Miller,[9,10] its extensions,[11,18] and applications to collision problems.[19,20] Meyer and Miller solve for the time-dependent coefficients of the electronic configurations that are selected, where the time dependence is due to the motion of the nuclei. We solve for the time-dependent coefficients of the site orbitals that are included in the basis set. The time dependence is twofold: one due to the purely electronic dynamics and one due to the motion of the nuclei. The distinction is not either−or because the electronic coupling terms depend on the nuclear positions. In other words, we diagonalize the electronic problem at the same time as we propagate the dynamics. When one can include all the configurations that are possible for a given basis set, and in the orbital approximation for the electronic Hamiltonian, the result of the two procedures will be the same (i.e., up to a canonical transformation). This is the case in any one-electron problem. Our method was introduced specifically for such problems where, due to strong electron correlations, there are innumerably more configurations than site basis functions.

One can consider avoiding some of the limitations of a classical description of the nuclear motion by treating electrons and nuclei in a similar way. In other words, by introducing basis functions (e.g., travelling Gaussians[21−25]) for the quantal nuclear motion and solving for the time-dependent weights of these nuclear basis states. This procedure also allows for introducing correlations between electronic and nuclear motion such that there is a different nuclear dynamics for different electronic states.[26] The resulting formalism is well-explored,[24,27,28] and here we are content with a classical description of the nuclear motion.

We discuss the dynamics of an electron exchange between two atomic sites, one orbital per site. The distance between the sites is allowed to vary subject to the total Hamiltonian. There are quantum mechanical, semiclassical, and classical methods that are available to treat this dynamical problem. Our aim is not to propose one more method for treating nonadiabatic atomic collisions. We are interested in the dynamics of the electron due to the coupling to the motion of the nuclei. Specifically we aim to demonstrate the possible failure of the electronic motion to be governed solely by the instantaneous positions of the nuclei.

The dynamical solution presents the electronic motion from a point of view that is different from what is usually done in quantum chemistry. We therefore discuss what to expect. Our procedure is analogous to what is sometimes referred to as ‘doing dynamics on the fly’. At every instant of time we allow both electrons and nuclei to update their coordinates according to the instantaneous values of the forces. It is worthwhile to point out that this adjustment needs to take place also in the dynamical regime where the Born−Oppenheimer separation is a good approximation. Indeed, one can think of the separation as the approximation where the faster moving electrons very rapidly adjust to the current position of the nuclei. In other words, also when the Born−Oppenheimer separation is a good approximation, the electrons constantly move. Furthermore, this motion takes place even when the electronic state is a stationary one. Superficially this may seem unreasonable. But one must bear in mind that the electronic state is a stationary one for a given, fixed, value of the nuclear coordinates. When the nuclei move to a new position, the (Born−Oppenheimer) electronic state can change because it depends parametrically on the nuclear coordinates. The signature of a failure of the Born−Oppenheimer separation is *not* that the site occupancy changes with time but that it changes with time not according to the dictate of the heavier and slower moving nuclei. In the case of an extreme failure of the Born−Oppenheimer approximation, it is the nuclear motion that rapidly adjusts to the instantaneous location of the electron.

In their original paper[29] Born and Oppenheimer argued, by perturbation theory, that the separation between the electronic and nuclear motion is governed by a coupling constant which is the ratio of the electron to nuclear masses, $\kappa^2 = \sqrt{m/\mu}$. Using the notion of mechanical similarity,[30] we shall show analytically that in the classical limit the electron−nuclear dynamics depends only on κ^2. Ordinarily, one is in the $\kappa^2 \ll 1$ limit. In high Rydberg states one encounters the ‘inverse’ Born−Oppenheimer regime[12] where the electron of very high principal quantum number has a very long orbital period, longer than vibrational or even rotational periods for the motion of the nuclei. We mimic the slow motion of the electron by computing the dynamics in the $\kappa^2 \gg 1$ limit, where the simulations show that the faster moving nuclei rapidly adjust to the instantaneous position of the electron.

The classical Hamiltonian is derived in section 2. Section 2 and Appendix A also provide a brief summary of those results of the quantum mechanical orbital approximation for H_2^+ that are needed for taking the classical limit. The equations of motion are set up and solved in section 3. Mechanical similarity and the scaling of the equations of motion in κ^2 are discussed in section 4 with more details provided in Appendix B.

2. Classical Limit for the One-Electron Two-Site Orbital Problem

For the quantum mechanical problem we follow the discussion of H_2^+ in Chapters 1 and 2 of Slater[31] with background details given in Appendix A. The electronic Hamiltonian in a basis of two orthogonal equivalent site orbitals is derived in Appendix A as

$$\mathbf{H}_{\mathrm{el}} = \begin{pmatrix} E_0(R) & \beta(R) \\ \beta(R) & E_0(R) \end{pmatrix} \tag{2.1}$$

Analytical expressions for the matrix elements and their dependence on the internuclear distance R are given in Appendix A and shown graphically in Figure 6 therein. For the electron-transfer integral $\beta(R)$ the simple declining exponential

$$\beta(R) = -\beta_0 \exp(-R/L) \tag{2.2}$$

provides an accurate fit at all but very close in distances. Unlike as in the Hückel approximation, the energy of a site $E_0(R)$ does vary, albeit weakly, with the site−site separation.

The classical limit for the electronic degrees of freedom[15,16] will be taken for the Hamiltonian (2.1). The classical variables are one pair of (conjugate) variables per orbital. We shall use the number n, $0 \leq n \leq 1$, of electrons per orbital, which is an action variable, and the conjugate phase ϕ. It will become clear that the electronic Hamiltonian conserves the number $n_a + n_b$ of electrons, where a and b are the indices of the sites. (Classically, this is because it is independent of the conjugate angle variable $\phi_a + \phi_b$.) Hence we require only two classical variables: the charge difference between the two sites $n = n_a - n_b$ (since $n_a + n_b = 1$) and the phase difference $\phi = \phi_a - \phi_b$. As is expected from the quantum mechanical Hamiltonian (2.1) and as will be shown classically explicitly, the two stationary electronic states are the two combinations in ($\phi = 0$) and out ($\phi = \pi$) of phase, respectively.

To obtain the classical limit of the Hamiltonian we first write the quantal Hamiltonian in second quantized form. Using creation $\hat{S}_{i+}$ and annihilation $\hat{S}_{i-}$ operators (denoted by a caret) for the electron on either site, $i = a$ or b

$$\hat{H}_{\mathrm{el}} = E_a(R)\hat{S}_{a+}\hat{S}_{a-} + E_b(R)\hat{S}_{b+}\hat{S}_{b-} + \beta(R)\hat{S}_{b+}\hat{S}_{a-} + \beta(R)\hat{S}_{a+}\hat{S}_{b-} \quad (2.3)$$

When the two sites are equivalent the two site energies $E_i(R)$ are identical. The classical limit is obtained by taking coherent states expectation values, where the coherent states need to be specially constructed to take care of the restrictions imposed by the Pauli principle.[15] For the simple case of one electron, see eq 2.13 of ref 16, one has

$$\langle \hat{S}_{i+}\hat{S}_{j-}\rangle_{\mathrm{cl}} = \langle \chi_{N=1}|\hat{S}_{i+}\hat{S}_{j-}|\chi_{N=1}\rangle = \exp(i(\phi_i - \phi_j))\sqrt{n_i n_j} \quad (2.4)$$

where the site index $i = a$ or b. The expectation value of the quantal Hamiltonian (2.1) is obtained, using eq 2.4, as

$$H_{\mathrm{el}}(R) \equiv \langle \hat{H}_{\mathrm{el}}\rangle = E_a(R)n_a + E_b(R)n_b + 2\beta(R)\sqrt{n_a n_b}\cos(\phi_a - \phi_b) \quad (2.5)$$

Note that the electronic energy depends not only on the population of the two sites but also on their relative phase. For a nonstationary electronic state, where the phases of the site occupancies vary rapidly with time, the dependence on the electronic phase is an additional source of modulation of the interaction.

In the general case the Hamiltonian (2.3) will contain terms up to fourth order in the electronic operators. It is then not the case that the expectation values of the higher order operators are the products of expectation values of linear and bilinear terms. In that sense, our procedure is a classical limit. For an orbital approximation, when the Hamiltonian has no terms beyond the bilinear ones, the transcription is an exact one.[16]

Equation 2.5 is just the electronic part. The full classical Hamiltonian contains two additional terms: the Coulomb repulsion between the nuclei $V_{nn}(R)$ and the kinetic energy for the relative motion, of reduced mass μ, of the two centers

$$H = P^2/2\mu + V_{nn}(R) + H_{\mathrm{el}}(R) \quad (2.6)$$

The dynamic coupling between the electronic and nuclear motions is evident from the terms that depend on both kinds of variables. Oscillations of charge from one site to another make the electronic energy, $H_{\mathrm{el}}(R)$ time-dependent. Then the nuclei are subject to a rapidly varying force, with a period determined by the migration of charge between the two sites. In the Born−Oppenheimer approximation one first determines the stationary, R-dependent solution of the electronic Hamiltonian and uses the expectation value of the electronic Hamiltonian as the potential for the motion of the nuclei. The breakdown is caused by a stationary solution of the electronic problem not necessarily being a stationary solution of the full Hamiltonian. The reason is that when the relative separation R is not a parameter of the Hamiltonian but a dynamical variable, the terms in the electronic Hamiltonian will be modulated as a function of time. Of course, the cross-modulation between the two motions will only be effective when they have comparable periods. Typically, the nuclear motion is much slower, and this is what allowed Born and Oppenheimer to introduce their separation. We shall use the reduced mass μ to scale the period ($\propto 1/\sqrt{\mu}$) of the nuclear motion, and we shall verify analytically that the dynamics depend only on the mass ratio

$$\kappa^4 = m/\mu \quad (2.7)$$

and not on the individual masses. Born and Oppenheimer[29] showed that κ^2 is the relevant perturbation parameter, and we will show analytically that the electron−nuclear dynamics only depends on this ratio. The absolute values of the masses are relevant since they determine the period of the motions. Hence if an external time scale, such as an electromagnetic field, is added to the Hamiltonian, then the absolute values of the masses do matter. But if there is no external frequency with which one can resonate then only the mass ratio needs to be specified.

The two-equivalent-site problem presents an interesting special case because the stationary solutions for the electronic motion, which have even or odd symmetry, remain stationary even when the charge-transfer amplitude β is modulated by the motion of the nuclei. We will therefore also show computational results for two in inequivalent sites.

Given the classical Hamiltonian, eqs 2.5 and 2.6, one can compute a unique classical trajectory for the relative motion of the nuclei and results are reported in section 3. However, for given electronic initial conditions, the dynamics can depend on the initial conditions chosen for the nuclear vibration. The reason is the back-coupling from the nuclear trajectory to the electronic dynamics. Therefore, in a manner made familiar by ordinary (sometimes called ‘quasi-classical’) trajectory computations, one can sample the initial phase of the vibration. In those situations, e.g., in Figure 5, where there can be energy transfer between the electronic and the nuclear degrees of freedom, the qualitative outcome of the dynamics does depend on the initial phase. It is then possible to compute a quasi-classical probability by running many trajectories in a narrow energy range and determining the fraction of all trajectories that lead to a particular outcome.

3. Equations of Motion

The classical Hamiltonian determines the time evolution for both electronic

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = -\frac{\partial H_{\mathrm{cl}}}{\partial \phi_i}, \quad \frac{\mathrm{d}\phi_i}{\mathrm{d}t} = \frac{\partial H_{\mathrm{cl}}}{\partial n_i}, \; i = a,b \quad (3.1)$$

and nuclear

$$\frac{\mathrm{d}P}{\mathrm{d}t} = -\frac{\partial H_{\mathrm{cl}}}{\partial R}, \quad \frac{\mathrm{d}R}{\mathrm{d}t} = \frac{\partial H_{\mathrm{cl}}}{\partial P} \quad (3.2)$$

degrees of freedom. For the Hamiltonian specified in eqs 2.5 and 2.6, it follows that any increase in the charge on one site is exactly compensated by a decrease in the other charge

$$\frac{\mathrm{d}n_a}{\mathrm{d}t}+\frac{\mathrm{d}n_b}{\mathrm{d}t}=0 \tag{3.3}$$

For this reason the coupling (charge-transfer) term in the electronic Hamiltonian can be referred to as a one−one resonance. Taking advantage of the conservation of the total charge (which we take to equal unity) one can reduce the number of classical variables for the electron dynamics to just two conjugate variables

$$n \equiv (n_a - n_b)/\sqrt{2},\ \phi \equiv (\phi_a - \phi_b)/\sqrt{2},\ \{n,\phi\} = 1 \tag{3.4}$$

The division by a factor of $\sqrt{2}$ is needed to make the variables canonically conjugate; that is, that their Poisson (curly) bracket is unity, as indicated. In this way the new variables satisfy Hamiltonian equations of motion

$$\frac{\mathrm{d}n}{\mathrm{d}t}=-\frac{\partial H_{\mathrm{cl}}}{\partial\phi},\ \frac{\mathrm{d}\phi}{\mathrm{d}t}=\frac{\partial H_{\mathrm{cl}}}{\partial n} \tag{3.5}$$

where eq 2.5 is expressed in terms of the new variables as

$$H_{\mathrm{el}}(R) = (E_a(R) + E_b(R))/2 + n(E_a(R) - E_b(R))/\sqrt{2} + \beta(R)\sqrt{1-2n^2}\cos(\phi\sqrt{2}) \tag{3.6}$$

For the two-equivalent-site problem, when the site energies are equal, the two stationary solutions of the electronic problem, $\mathrm{d}n/\mathrm{d}t = 0$, $\mathrm{d}\phi/\mathrm{d}t = 0$, are obtained when $\cos(\phi\sqrt{2}) = \pm 1$. These are the classical even and odd solutions. The classical Born−Oppenheimer approximation is obtained by computing the classical electronic energy as a function of the parameter R. For the two stationary electronic states the value of the energy is $H_{\mathrm{el}}(R) = E_{\mathrm{g}}(R)$ or $E_{\mathrm{u}}(R)$.

The full classical Hamiltonian for two identical sites is

$$H_{\mathrm{cl}} = E_0(R) + \beta(R)\sqrt{1-2n^2}\cos(\sqrt{2}\phi) + 1/R + P^2/2\mu \tag{3.7}$$

with

$$E_0(R) = (E_{\mathrm{g}}(R) + E_{\mathrm{u}}(R))/2,\ \beta(R) = (E_{\mathrm{g}}(R) - E_{\mathrm{u}}(R))/2 \tag{3.8}$$

as shown in the Figure 6 in Appendix A. The four equations of motion that we solve are

$$\frac{\mathrm{d}n}{\mathrm{d}t}=\sqrt{2}\,\beta(R)(1-2n^2)^{1/2}\sin(\sqrt{2}\phi) \tag{3.9}$$

$$\frac{\mathrm{d}\phi}{\mathrm{d}t}=-2n\beta(R)(1-2n^2)^{-1/2}\cos(\sqrt{2}\phi) \tag{3.10}$$

$$\frac{\mathrm{d}R}{\mathrm{d}t}=P/\mu \tag{3.11}$$

$$\frac{\mathrm{d}P}{\mathrm{d}t}=-\frac{\mathrm{d}E_0(R)}{\mathrm{d}R}+\frac{1}{R^2}-(1-2n^2)^{1/2}\cos(\sqrt{2}\phi)\frac{\mathrm{d}\beta(R)}{\mathrm{d}R} \tag{3.12}$$

The equation of motion for the nuclei has two parts. The first two terms are the mean potential of the two electronic states. The third term is however determined not just by the population of the two sites $(1-2n^2)^{1/2} = 2\sqrt{n_a n_b}$ but also by their (time-dependent and coupled to the R motion, eq 3.10) relative phase.

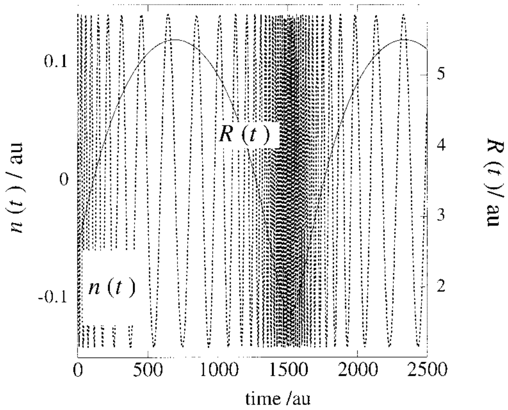

Figure 1. Exactly computed electron (dotted curve) and nuclear (full curve) dynamics vs time in the Born−Oppenheimer regime. Note how the electronic motion is much faster and how its period tracks the position of the nuclei. This is because, as shown in Figure 6, the electronic coupling, $\beta(R)$, is a rapidly varying function of R. In the text we show that the dynamics is completely defined by the ratio, κ^{-4}, of the reduced mass of the nuclei to the mass of the electron, eq 4.2. This plot is for $\kappa = 0.1778$. The action variable n is in units of $\hbar$.

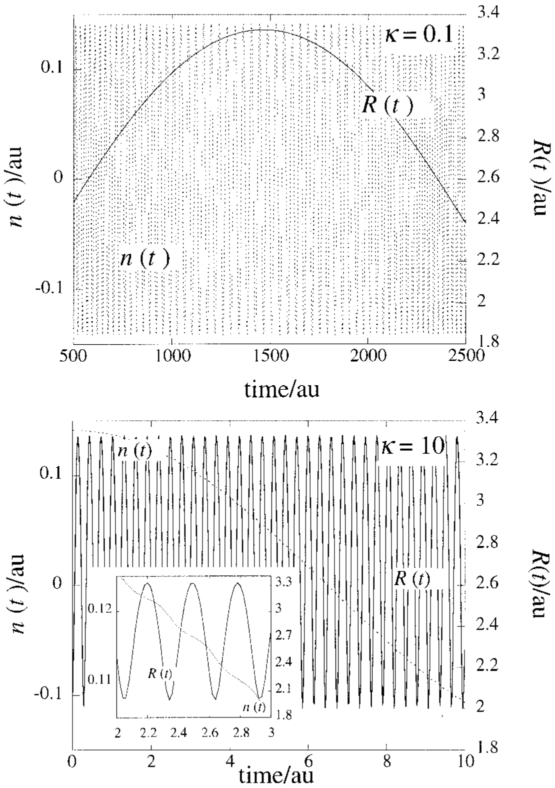

Figure 2. Exactly computed electron (dotted curve) and nuclear (full curve) dynamics vs time in the Born−Oppenheimer regime (top panel) and in its inverse (bottom panel). In the inverse regime the faster moving nuclei adjust rapidly to the electron. The staircase-like motion of the slow electron vs time, which is seen upon the close examination provided by the insert, is discussed in the text.

Figure 1 shows typical trajectories in the Born−Oppenheimer ($\kappa^4 \ll 1$) regime. The overall point is that the electronic motion is far faster than that of the nuclei. There is also a more detailed point namely that the electronic motion ‘instantly’ adjusts to the location of the nuclei. The latter is the essence of the Born−Oppenheimer separation. To make this point in a graphically vivid manner we chose initial conditions for the nuclear motion such that its amplitude is reasonably high. This motion is shown as the solid line with its scale on the ordinate on the right. The wide variations in R imply, cf. Figure 2, that the transfer integral $\beta(R)$ varies by more than 1 order of magnitude. At a given R the frequency of the electronic motion between two equivalent sites is $2\beta(R)$. Therefore, if the electron fully tracks the motion of the nuclei, its frequency will be quite high when the two atoms are near and quite low when the atoms are far apart. In this adiabatic regime, the nuclear dynamics are very accurately given by solving, as usual, for the nuclear motion in the ground electronic potential $E_g(R)$.

One has decades of experience that usually, and certainly for H_2^+, the Born−Oppenheimer separation works very well for the nuclear motion in the ground electronic state. Therefore, the result that the ordinary vibrational motion computed on the ground electronic potential is, in the Born−Oppenheimer ($\kappa^4 \ll 1$) regime, identical to computing a nuclear trajectory using the coupled dynamics can be considered as a test of the method.

Figure 2 contrasts the numerical solution of the equations of motion in the Born−Oppenheimer ($\kappa = 0.1$) and inverse Born−Oppenheimer ($\kappa = 10$) regimes. That the two limits are complementary is quite clear from the numerical results. In the Born−Oppenheimer regime the slowly moving nuclei determine the instantaneous value of $\beta(R)$ and the electrons immediately adjust to this value of the transfer integral. In the inverse regime, the fast moving nuclei immediately adjust to the local position of the electrons. This leads to an interesting aspect that is only seen when the abscissa is blown up. As seen in the insert, the electronic motion vs time is a staircase-like curve. The reason is the long time that a vibrational motion in an anharmonic potential spends at the outer turning point. Therefore, there are relatively long time windows where $R(t)$ is large. During those windows the coupling $\beta(R)$ is very small, and so the electronic charge distribution is not changing.

An interesting feature of the numerical solution, which deserves a separate discussion that will be given elsewhere, is that the breakdown of the Born−Oppenheimer approximation is much more prominent when the electronic state itself is not stationary. In the special case of two equivalent sites, this is easier to understand. The Born−Oppenheimer stationary electronic state has $n = 0$ irrespective of the value of $\beta(R)$. When the two sites are not equivalent, the term $n(E_a(R) - E_b(R))/\sqrt{2}$ in eq 3.6 is not vanishing and so the phase is more rapidly varying. For us, the unexpected point is that the separation of the electronic and nuclear motions is less accurate when the initial electronic state is not a Born−Oppenheimer stationary state.

An example of electron dynamics for two inequivalent sites is shown in Figure 3. In the Born−Oppenheimer separation one solves the electron dynamics for clamped nuclei. In our case this means that for each value of time one uses the value of the instantaneous separation R to get the value of the electronic coupling. The resulting expression for the charge migration is $n(t) = -(\Delta\alpha/\sqrt{2})((\Delta\alpha)^2 + (2\beta(R(t)))^2)^{-1/2}$. This works even for not too low values of κ, but fails, as shown in Figure 3, when $\kappa > 1$.

Figure 4 shows an example of the breakdown of the separation of the two motions. The initial conditions for the motion of the nuclei ($(R(0),P(0))$) are chosen such that in the Born−Oppenheimer approximation, it corresponds to a high bound vibrational state. The motion in the Born−Oppenheimer approximation is plotted at discrete values of time. The continuous curve that goes through these points is the trajectory computed from the fully coupled dynamics. The full dynamics requires specifying initial values also for the electronic motion, and the bound trajectory shown in Figure 4 is for the system initially in the ground electronic state ($n(0) = 0, \phi(0) = 0$). Suppose however that the initial electronic state is not quite stationary. Then the transfer of electronic energy to the nuclear motion is quite facile and within one-half of a nuclear period the bond dissociates.

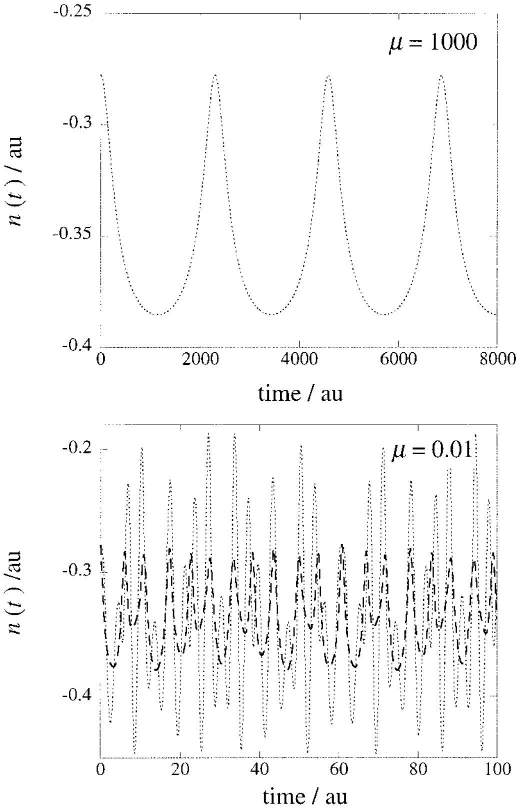

Figure 3. Exactly computed electron (dotted curve) dynamics vs time in the Born−Oppenheimer regime (top panel) and in its inverse (bottom panel) for two sites which differ considerably in their ionization potentials ($\Delta IP = \beta(R_{eq})$). The electron stays longer at one site than the other. For each panel, one can analytically solve the electron dynamics in the Born−Oppenheimer separation. For the top panel, $\kappa = 0.1778$, the result is distinguishable from the exact dynamics but is barely different to graph reading accuracy. For the bottom panel, $\kappa = 3.162$, and then the Born−Oppenheimer separation (dashed curve) fails.

Figure 5 shows the trajectory of the electron for the dissociating trajectory shown in Figure 4. At early times when the motion is Born−Oppenheimer like, cf. Figure 4, the electron rapidly adjusts to the motion of the nuclei, hopping back and forth between them. Then the electron stayed too long on one side of the molecule, and this allowed the bond to break.

4. Mechanical Similarity

Mechanical similarity[30] is a theorem about the invariance of the equations of motion of classical mechanics. The familiar virial theorem, long a mainstay of electronic structure theory,[32,31] is a special case for a stationary bounded system. We here use a special case of the general result in order to show that systems with a given value of $\kappa^2 \equiv \sqrt{m/\mu}$ follow the same trajectories.

The identification of κ^2 as the parameter whose (small) value allows for a separation of the electronic and nuclear motion is due to Born and Oppenheimer.[29] They did so by casting the full quantum mechanical stationary solution as a perturbation expansion with κ^2 as the coupling parameter. We shall show explicitly that in the classical limit the full dynamics is governed by the magnitude of κ^2.

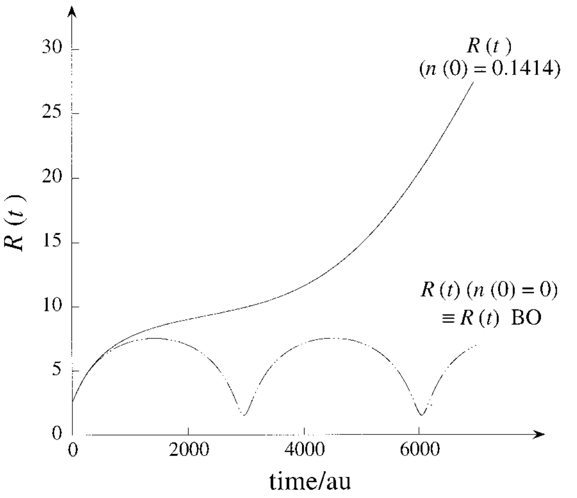

Figure 4. Example of a qualitative breakdown of the Born−Oppenheimer separation. $\kappa = 0.1778$. Shown are three nuclear trajectories, all three starting from the same initial conditions, R at equilibrium and a high momentum. When the initial conditions for the electron correspond to a (Born−Oppenheimer) stationary state, $n = 0$ for a symmetric diatomic, the motion remains bound. The solution for $R(t)$ in the Born−Oppenheimer approximation (short-dashed curve) cannot be distinguished from the results of the exact dynamics (long-dashed curve). If the initial electronic state is not stationary so that there is some electronic energy over the ground state, then energy rapidly flows into the nuclear motion and the molecule dissociates. The corresponding electron dynamics are shown in Figure 5.

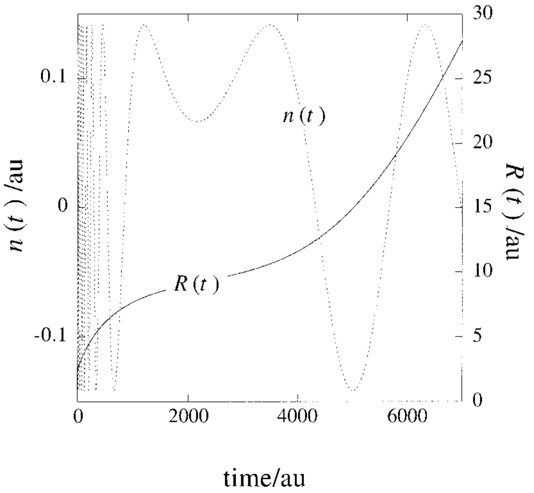

Figure 5. Electron dynamics (dotted line) for the dissociating trajectory shown in Figure 4 and reproduced also in this figure. When the nuclear motion is bound, the period of the electronic motion is quite short. At about 1000 au of time, when the electron is on one side of the molecule, it fails to swing to the other side and instead imparts energy to the nuclear motion.

Superficially, it may seem that there is no need for a detailed proof and that the following general argument will do: Consider a Newtonian problem with n degrees of freedom, each with its own mass. Then the equations of motion for the coordinates are $m_i \mathrm{d}^2 r_i/\mathrm{d}t^2 = -\partial V/\partial r_i$, $i = 1,...,n$. If all masses are scaled by a common factor κ^4 the equations of motion and their solution remain unchanged except that time runs faster by the factor κ^2. Q.E.D. The reason one cannot simply refer to this well-known result is that the mechanical coordinates of the electron have also kinetic and not only potential coupling, the two together being necessary to have a strict one-one resonance coupling of the type exhibited in the Hamiltonian (3.6). So we regard it as unavoidable to verify the result. We provide a shorter proof in the text and a completely detailed proof in Appendix B.

The short proof begins with the observation that since we work in atomic units, all masses are measured in units of the electron mass. Therefore the equation of motion for the nuclei, eqs 3.11 and 3.12, should really be written as

$$\kappa^{-4}\frac{\mathrm{d}^2R}{\mathrm{d}t^2} = -\frac{\mathrm{d}E_0(R)}{\mathrm{d}R} + \frac{1}{R^2} - (1-2n^2)^{1/2}\cos(\sqrt{2}\phi)\frac{\mathrm{d}\beta(R)}{\mathrm{d}R} \tag{4.1}$$

The equations of motion for the action-angle variables, eqs 3.9 and 3.10, remain as they are when expressed in atomic units. Therefore, the only dependence on κ is in the left-hand side of eq 3.11. The left-hand side of eq 4.1 suggests that time is scaled by κ^2, $\tau = \kappa^2 t$, so that the nuclear dynamics become independent of the mass

$$\frac{\mathrm{d}^2R}{\mathrm{d}\tau^2} = -\frac{\mathrm{d}E_0(R)}{\mathrm{d}R} + \frac{1}{R^2} - (1-2n^2)^{1/2}\cos(\sqrt{2}\phi)\frac{\mathrm{d}\beta(R)}{\mathrm{d}R} \tag{4.2}$$

Numerically, if one solves the unscaled equation of motion (3.11) for $R(t)$ then trajectories computed for different values of μ should fall on the same curve when plotted vs τ. We have verified that this is the case for the results for $R(t)$ where between the two panels shown in Figure 2 the value of μ is changed by 8 orders of magnitude. The reader will quickly recognize that the equations of motion (3.9, 3.10) for the electron do not scale with τ . This is only apparently so because the equations are written in atomic units. In fact, they do scale properly but to show this one should be careful with the units. A continuation of the short proof is to note that if the action variable n is taken to be dimensionless (i.e., it is action measured in units of $\hbar$) then the coupling integral β in eq 3.9 has the dimensions of frequency while in eq 2.5 it has the dimensions of energy. In other words, to be precise with the units, the coupling in eq 3.9 should be written as $(\beta(R)/\hbar)$ (the same is true for eq 3.10). The scaled equation of motion for n therefore reads

$$\frac{\mathrm{d}n}{\mathrm{d}\tau} = \sqrt{2}\,(\beta(R)/\hbar^*)(1-2n^2)^{1/2}\sin(\sqrt{2}\phi) \tag{4.3}$$

where $\hbar^*$ is the value of Planck's constant for the new value of the electronic mass. In other words, we take the value of Planck's constant to change if we change the mass of the electron. The reason is that in doing mechanics one is allowed to scale the mass while keeping the length unchanged. So when, say, the Bohr radius is kept constant and the electron mass is scaled, then it is inevitable that $\hbar$ scales as $\sqrt{m}$ and frequency scales as $1/\sqrt{m}$. When time is scaled with $\sqrt{m}$ then energy is unchanged. Appendix B gives a more detailed discussion.

5. Concluding Remarks

Coupled electronic and nuclear classical equations of motion for an electron oscillating between two centers were presented and solved numerically. The electron transfer between the two sites is governed by the electronic interaction. This interaction is a function of the site−site distance, and this couples the electronic and nuclear motions. We work in the site representation so that the electronic motion does not cease even if the nuclei are clamped. As expected, when the nuclear motion is slow compared to the electronic hopping between the two sites, the Born−Oppenheimer separation works well: the period of the electronic motion is determined by the value of the electronic coupling for the nuclei clamped at that point and the nuclear motion is governed by a static potential determined as the eigenvalue of the electronic problem for clamped nuclei. The coupled classical equations of motion depend only on the ratio of electronic to nuclear mass, $\kappa^4 = m/\mu$. For $\kappa < 1$, the Born–Oppenheimer separation works well except when the initial charge distribution is far from a stationary one (e.g., asymmetric for two equivalent sites). For $\kappa > 1$, the separation fails and it is the electron that moves in the static potential determined by the nuclei.

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Appendix A: Quantum Chemistry

The elementary discussion of H_2^+ (Chapters 1 and 2 of Slater[31]) begins with hydrogenic orbitals, eq A.1, one orbital per site. For a finite site−site separation R, such orbitals are not orthogonal and their overlap, which depends on R, is denoted by S. The equivalent-two-site problem has an inversion symmetry and so linear combination of orbitals can be given an even (g) or odd (u) symmetry labels. When only one orbital is used per site, the two states are

$$\sigma_{g/u} = [(2\pi/\alpha^3)(1 \pm S)]^{-1/2}(\exp(-\alpha r_a) \pm \exp(-\alpha r_b)) \quad (A.1)$$

Here r is the distance of the electron to its nucleus, with a screening constant α. We keep α explicitly for future reference but unless otherwise stated, the computations will be carried out for α fixed at the value of the separated atoms, $\alpha = Zme^2/\hbar^2$, where Z is the charge on the nucleus, and m and e are the electron's mass and charge. In the atomic units that we will use $\alpha = 1$, but since we intend to also discuss the scaling with the electron's mass, we show it explicitly.

In the limited atomic basis, the functions (A.1) diagonalize the Hamiltonian, with R-dependent eigenvalues, $E_{g/u}(R)$. Explicitly,

$$E_{g/u}(R) = (Ze^2\alpha)[F_1(\alpha R) + F_2(\alpha R)] \quad (A.2)$$

the first term being the kinetic energy and the second the potential. Our result differs from the form given by Slater in that we use an explicit form for the kinetic energy of the electron, namely $-(\hbar^2/2m)\nabla^2$, whereas Slater who works in Rydberg units writes the kinetic energy just as $-\nabla^2$. The F's are ratios of simple polynomials given explicitly by Slater. Making a few sign changes in these polynomials produces the expression for $E_u(R)$ so that using upper/lower signs for the g/u case respectively, in atomic units,

$$\begin{aligned} F_1(\alpha R) &= (1 \pm \exp(-\alpha R)(1 + \alpha R - (\alpha R)^2/3))/2(1 \pm S) \\ F_2(\alpha R) &= -(1 \pm 2\exp(-\alpha R)(1 + \alpha R) + (1/\alpha R) - \\ &\qquad \exp(-2\alpha R)(1 + 1/\alpha R))/(1 \pm S) \end{aligned} \quad (A.3)$$

where S is the overlap integral

$$S(\alpha R) = \exp(-\alpha R)(1 + \alpha R + (\alpha R)^2/3) \quad (A.4)$$

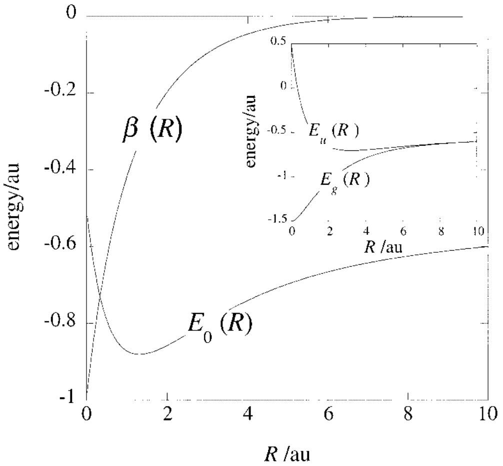

Figure 6. Electron-transfer coupling, $\beta(R)$, and the site electronic energy, $E_0(R)$, as defined in eq 3.8. Note the essentially exponential decline of $\beta(R)$ with the internuclear separation R. In the Born−Oppenheimer approximation $2\beta(R)/\hbar$ is the frequency of the electronic motion when the two nuclei are at the distance R apart. As discussed in Appendix B, this frequency decreases, as $1/\sqrt{m}$, when the electronic mass m is (artificially) increased. The insert shows the two eigenvalues, of even and odd symmetry, of the electronic Hamiltonian of H_2^+ vs the internuclear distance R. Note that the Coulomb repulsion between the two nuclei is not included in the values as shown. The potential energy for the nuclei is, in the Born−Oppenheimer approximation, $E(R) + 1/R$. The eigenvalues are computed without optimizing the screening parameter α.

To assign the charge uniquely to one site or the other, we de-diagonalize the electronic Hamiltonian. For two equivalent sites this is achieved by a rotation of 45°

$$\mathbf{H}_{el} = \begin{pmatrix} E_g(R) & \\ & E_u(R) \end{pmatrix} \xrightarrow{\text{rotation}} \begin{pmatrix} E_0(R) & \beta(R) \\ \beta(R) & E_0(R) \end{pmatrix} \quad (A.5)$$

The orthogonal site orbitals in which the new Hamiltonian matrix is specified are

$$\varphi_{a/b} = (\sigma_g \pm \sigma_u)/\sqrt{2} \text{ or } \sigma_{g/u} = (\varphi_a \pm \varphi_b)/\sqrt{2} \quad (A.6)$$

and correspond to the orthogonalized basis orbitals of Löwdin.[33] The migration of charge from one site to another is due to the transfer amplitude β,

$$\beta(R) = \langle \varphi_a | H_{el} | \varphi_b \rangle = (E_g(R) - E_u(R))/2 \quad (A.7)$$

Equations A.2−A.7 provide an analytic expression for the dependence of the electron-transfer amplitude on the internuclear distance R, a dependence that is well-fitted as a simple exponential, eq 2.2. (The correlation coefficient for $R > 0.3$ au is better than 0.999, and a sum of two exponentials provides an essentially exact fit for $\beta(R)$.) Figure 6 is a plot of the analytic form of $\beta(R)$ as well as that of the site energy, $E_0(R) = \langle \varphi_a | H_{el} | \varphi_b \rangle$. Note that the simple Hückel approximation takes the site energy to be independent of the distance to the other site. This is not exactly the case, as shown in Figure 6. The deviation of the site energy from the value of an isolated site is accurately represented as a difference of two exponentials.

Appendix B: Scaling

We want to scale time and mass but not distance such that Newton's equation of motion and therefore energy, remain unchanged. If the potential energy is only a function of the coordinates, it is unchanged by such a scaling. The kinetic energy is unchanged if the mass and time are changed such that mass/time^2 remains constant. We first complete all the details for the discussion given in the text in section 4[34] and then give a proof purely within classical mechanics without a reference to $\hbar$.

The atomic unit of energy[34] e^2/a, where a is the Bohr radius and e the elementary charge, remains unchanged under the proposed scaling. The atomic unit of frequency $e^2/a\hbar$ will change and requires that if the mass of the electron is changed, we scale the value of $\hbar$ such that, using primes for the new values, $\hbar = (m'/m)^{1/2}\hbar$. As a check note that this scaling keeps the value of the dimensionless fine structure constant $e^2/\hbar c$, where c is the velocity of light. (The scaling of time requires that $c' = (m'/m)^{-1/2}c$.) The atomic unit of time, $\hbar^3/me^4$, scales with $\sqrt{m}$ as it should. This provides all the details needed to rescale equations written in atomic units. There is however no essential need to work in atomic units. Indeed, they are a shade cumbersome if one wants to scale the mass of the electron. Therefore we provide a proof of mechanical similarity without any reference to the value of Planck's constant.

Let I be a classical action variable. The classical electronic Hamiltonian, written in terms of dimension bearing action variables is, cf. eq 2.5

$$H_{\mathrm{el}}(R) = \omega_a(R)I_a + \omega_b(R)I_b + 2\omega(R)\sqrt{I_aI_b}\cos(\phi_a - \phi_b) \tag{B.1}$$

The different frequencies that appear in eq B.1 correspond to the energies that appear in eq 2.5. As in the text, we put $I_a + I_b = A$, $I_a - I_b \equiv \sqrt{2}\, I$ so that the equation of motion for I is

$$\frac{\mathrm{d}I}{\mathrm{d}t} = \sqrt{2}\,\omega(R)(A^2 - 2I^2)^{1/2}\sin(\sqrt{2}\phi) \tag{B.2}$$

An action variable, dimensions coordinate·momentum, scales as mass/time and since $t' = (m'/m)^{1/2}t$, $I' = (m'/m)^{1/2}I$. Therefore the left-hand side of eq B.2 is unchanged by the scaling, $(\mathrm{d}I/\mathrm{d}t)' = (\mathrm{d}I/\mathrm{d}t)$. The right-hand side is unchanged because the frequency scales as 1/time.

An even longer derivation begins with the actual coordinate and momentum of the electron with respect to the two sites and expresses the Hamiltonian in terms of them. For completeness sake we write the form of such a Hamiltonian for two equivalent sites, using lower case fonts for the variables that describe the electronic motion:

$$H_{\mathrm{cl}}(R) = \frac{1}{2}k{r_a}^2 + \frac{1}{2m}{p_a}^2 + \frac{1}{2}k{r_b}^2 + \frac{1}{2m}{p_b}^2 + \omega(R)m\bar{\omega}\, r_ar_b + \omega(R)\frac{p_ap_b}{m\bar{\omega}} + E_0(R) + \frac{1}{R} + \frac{P^2}{2\mu} \tag{B.3}$$

where the frequency for the motion of the electron is given by

$$\bar{\omega} = \sqrt{k/m} \tag{B.4}$$

The equation of motion for R is

$$\mu\frac{\mathrm{d}^2R}{\mathrm{d}t^2} = \kappa^{-4}\frac{\mathrm{d}^2R}{\mathrm{d}\tau^2} = -m\bar{\omega}\, r_ar_b\frac{\mathrm{d}\omega(R)}{\mathrm{d}R} - \frac{p_ap_b}{m\bar{\omega}}\frac{\mathrm{d}\omega(R)}{\mathrm{d}R} - \frac{\mathrm{d}E_0(R)}{\mathrm{d}R} + \frac{1}{R^2} \tag{B.5}$$

so that the nuclear motion only depends on κ. From eq B.5 $\tau = t/\sqrt{m}$. The equation of motion for r_a is

$$m\frac{\mathrm{d}^2r_a}{\mathrm{d}t^2} = \frac{d^2r_a}{d\tau^2} = -kr_a - \omega(R)\bar{\omega}mr_b - \frac{\omega(R)}{\bar{\omega}}kr_b - \omega(R)^2mr_a + \frac{p_b}{\bar{\omega}}\frac{\mathrm{d}\omega(R)}{\mathrm{d}R}\frac{1}{\sqrt{m}}\frac{\mathrm{d}R}{\mathrm{d}\tau} \tag{B.6}$$

where the right-hand side is also independent of the masses.

References and Notes

(1) Köppel, H.; Domcke, W.; Cederbaum, L. S. *Adv. Chem. Phys.* **1984**, *57*, 59.

(2) Yarkony, D. R. *Rev. Mod. Phys.* **1996**, *68*, 985.

(3) Desouter-Lecomte, M.; Dehareng, D.; Leyh-Nihant, B.; Praet, M. T.; Lorquet, A. J.; Lorquet, J. C. *J. Phys. Chem.* **1985**, *89*, 214.

(4) Born, M.; Huang, K. *Dynamical Theory of Crystal Lattice*; Oxford University Press: New York, 1988.

(5) Born, M. *Gött. Nachr. Math. Phys. Kl.* **1951**, 1.

(6) Deumens, E.; Diz, A.; Longo, R.; Ohrn, Y. *Rev. Mod. Phys.* **1994**, *66*, 917.

(7) Micha, D. A. *J. Phys. Chem. A* **1999**, *103*, 7562.

(8) Broeckhove, J.; Claessens, M.; Lathouwers, L.; Vanleuven, P.; Deumens, E.; Ohrn, Y. *J. Chem. Phys.* **1990**, *93*, 8945.

(9) Meyer, H.-D.; Miller, W. H. *J. Chem. Phys.* **1979**, *70*, 3214.

(10) Meyer, H.-D.; Miller, W. H. *J. Chem. Phys.* **1979**, *72*, 2272.

(11) Sun, X.; Miller, W. H. *J. Chem. Phys.* **1997**, *106*, 6346.

(12) Remacle, F.; Levine, R. D. *Int. J. Quantum Chem.* **1998**, *67*, 85.

(13) Schatz, G. C.; Ratner, M. A. *Quantum Mechanics in Chemistry*; Prentice Hall: New York, 1993.

(14) Kerner, E. H. *Phys. Rev. Lett.* **1959**, *2*, 152.

(15) Levine, R. D. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 1965.

(16) Remacle, F.; Levine, R. D. *J. Chem. Phys.* **2000**, *113*, 4515.

(17) Miller, W. H.; White, K. A. *J. Chem. Phys.* **1986**, *84*, 5059.

(18) Thoss, M.; Stock, G. *Phys. Rev. A* **1999**, *59*, 64.

(19) Meyer, H.-D.; Miller, W. H. *J. Chem. Phys.* **1979**, *71*, 2156.

(20) Currier, R.; Herman, M. F. *J. Chem. Phys.* **1985**, *82*, 4509.

(21) Adhikari, S.; Billing, G. D. *Chem. Phys. Lett.* **1999**, *309*, 249.

(22) Billing, G. D. *J. Chem. Phys.* **1999**, *110*, 5526.

(23) Heller, E. J. *J. Chem. Phys.* **1975**, *62*, 1544.

(24) Martinez, T. J.; Ben-Nun, M.; Levine, R. D. *J. Phys. Chem.* **1996**, *100*, 7884.

(25) Shin, S.; Metiu, H. *J. Phys. Chem.* **1996**, *100*, 7867.

(26) Ben-Nun, M.; Levine, R. D. *Chem. Phys.* **1995**, *201*, 163.

(27) Ben-Nun, M.; Quenneville, J.; Martinez, T. J. *J. Phys. Chem. A* **2000**, *104*, 5161.

(28) Ben-Nun, M.; Martinez, T. J. *J. Chem. Phys.* **2000**, *112*, 6113.

(29) Born, M.; Oppenheimer, R. *Ann. Phys.* **1927**, *84*, 457.

(30) Landau, L. D.; Lifshitz, E. M. *Mechanics*; Pergamon: Oxford, 1960.

(31) Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1963.

(32) Pilar, F. L. *Elementary Quantum Chemistry*; McGraw-Hill: New York, 1968.

(33) Lowdin, P. O. *J. Chem. Phys.* **1950**, *18*, 365.

(34) Bethe, H. A.; Salpeter, E. E. *Quantum Mechanics of One- and Two-Electron Atoms*; Plenum-Rosetta: New York, 1977.