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Brief Reports

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Electron-ion dynamics: A technique for simulating both electronic transitions and ionic motion in molecules and materials

Roland E. Allen
Department of Physics, Texas A&M University, College Station, Texas 77843

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We describe a technique for simultaneously treating the dynamics of electrons and ions. The key features are a generalized Hellmann-Feynman theorem, a standard time-dependent self-consistent-field (TDSCF) description, and use of the interaction picture to separate fast electronic oscillations from slower processes. The technique can be used in tight-binding or first-principles simulations, with either a ground-state or TDSCF Hamiltonian.

Classical,[1-7] tight-binding,[8-12] and first-principles[13-26] molecular-dynamics simulations have been used to address a wide variety of problems in chemistry and materials science. Here we introduce a much more general technique which can be used to treat the dynamics of electrons and ions simultaneously. Possible applications include absorption and emission of radiation, collisions of energetic atoms, carrier dynamics, and excited-state chemistry. The essential idea is to solve the time-dependent Schrödinger equation for the electrons, together with an effective Newton's equation for the ions. Three key features of the technique allow this to be accomplished in feasible numerical simulations.

(a) A generalized Hellmann-Feynman theorem

$$M\frac{d^2}{dt^2}\langle X\rangle=-\left\langle\frac{\partial\mathcal{H}}{\partial X}\right\rangle , \tag{1}$$

where X and M are any ion coordinate and mass. The expectation value is taken in the time-dependent state of the system, with the electrons in excited states and undergoing transitions.

(b) A time-dependent self-consistent-field description, with an equation of motion

$$i\hbar\partial\Psi_k/\partial t=H(t)\Psi_k \tag{2}$$

obtained by writing the electron field operator in the approximate form

$$\hat{\Psi}(\mathbf{r},t)=\sum_k\hat{a}_k\Psi_k(\mathbf{r},t) . \tag{3}$$

In this description, the generalized Hellmann-Feynman theorem (1) reduces to

$$M\frac{d^2}{dt^2}\langle X\rangle=-\sum_k n_k\int d^3r\,\Psi_k^*(\mathbf{r},t)\left\langle\frac{\partial H}{\partial X}\right\rangle\Psi_k(\mathbf{r},t)+F_{\rm ii}+F_{\rm ext} . \tag{4}$$

Each occupation number n_k is equal to zero or 1 and is constant in time. When the ion coordinates are treated classically, the angular brackets may be removed in (4) and on the left-hand side of (1).

(c) Use of the interaction picture in treating the effective time-dependent Schrödinger equation (2). Since electrons can move much faster than ions (on a femtosecond rather than picosecond time scale), direct solution of (2) in a simulation would require a very short time step. Instead we represent $\Psi_k(\mathbf{r},t)$ by the eigenstates of some time-independent reference Hamiltonian H_0: in Dirac notation,

$$|kt\rangle=\sum_n c_n(t)e^{-i\varepsilon_n t/\hbar}|n\rangle , \tag{5}$$

$$H_0|n\rangle=\varepsilon_n|n\rangle . \tag{6}$$

This separates the fast oscillations of $\exp(-i\varepsilon_n t/\hbar)$ from the slower time evolution $c_n(t)$ associated with electronic transitions. We can then analytically integrate the fast oscillations over each time step Δt.

We will first establish a framework that is suitable for *ab initio* calculations in the coordinate representation, and then obtain the corresponding results for tight-binding calculations with a nonorthogonal basis.

Let us begin by proving the generalized Hellmann-Feynman theorem, which is also the generalization of Ehrenfest's theorem to a system of ions and electrons. The proof employs the Heisenberg equation of motion

$$i\hbar\frac{dA}{dt}=[A,\mathcal{H}] \tag{7}$$

together with the identities[27]

$$[X,F]=i\hbar\frac{\partial F}{\partial P} , \quad [P,G]=-i\hbar\frac{\partial G}{\partial X} , \tag{8}$$

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where X is any ion coordinate and P is the conjugate momentum. A, F, and G are Heisenberg operators, and $\mathcal{H}$ is the full Hamiltonian of the system:

$$\mathcal{H}=\sum_l \frac{\mathbf{P}_l^2}{2M_l}+\sum_j \frac{\mathbf{p}_j^2}{2m}+\mathcal{H}_{\rm ii}+\mathcal{H}_{\rm ee}+\mathcal{H}_{\rm ei}+\mathcal{H}_{\rm ext} , \qquad (9)$$

$$\mathcal{H}_{\rm ii}=\sum_{l>l'} v_{ll'}(\mathbf{R}_l-\mathbf{R}_{l'}) , \qquad (10)$$

$$\mathcal{H}_{\rm ee}=\sum_{j>j'} v(\mathbf{r}_j-\mathbf{r}_{j'}) , \qquad (11)$$

$$\mathcal{H}_{\rm ei}=\sum_{jl} v_l(\mathbf{r}_j-\mathbf{R}_l) , \qquad (12)$$

with $\mathcal{H}_{\rm ext}$ representing the interaction of electrons and ions with external fields. Also, l and j respectively label ions and electrons, and each coordinate and momentum is regarded as a Heisenberg operator. The two equations in (8) give $\dot{X}=P/M$ and $\dot{P}=-\partial\mathcal{H}/\partial X$, or

$$M\frac{d^2X}{dt^2}=-\frac{\partial\mathcal{H}}{\partial X} . \qquad (13)$$

This is an operator equation, and we can now take the expectation value of both sides of the equation to obtain (1). Since expectation values are the same in any picture, (1) can also be interpreted in the Schrödinger picture, with time-independent operators and a time-dependent state.

Only three terms in (9) actually depend on X, so (1) has the alternative form

$$M\frac{d^2}{dt^2}\langle X\rangle=-\left\langle\frac{\partial\mathcal{H}_{\rm ei}}{\partial X}\right\rangle+F_{\rm ii}+F_{\rm ext} , \qquad (14)$$

where $F_{\rm ii}$ and $F_{\rm ext}$ are the forces due to other ions and external fields. In the simplest case, all the interactions of (10)–(12) are just Coulomb interactions: $v_{ll'}(\mathbf{r})=-Z_{l'}v_l(\mathbf{r})=Z_{l'}Z_l v(\mathbf{r})$, $v(\mathbf{r})=e^2/|\mathbf{r}|$. Then the $\mathcal{H}_{\rm ei}$ term in (14) is just the Coulomb attraction between electrons and ions, and $F_{\rm ii}$ is the ion-ion Coulomb repulsion. Expressed this way, our generalized Hellmann-Feynman theorem is just as "obvious" as the original theorem for the ground state and other eigenstates.

The standard time-dependent self-consistent-field (TDSCF) approximation can be derived from a variational principle,[28,29] but with the ions included it is convenient to use a less conventional derivation, which involves substituting (3) into the Heisenberg equation of motion (7). This approach is similar to a well-known derivation of static Hartree-Fock,[30] except that the coefficients Ψ_k are time dependent (and the $\hat{a}_k$ are Schrödinger operators). One can in fact follow the derivation on pp. 80–82 of Ref. 30, down to Eq. (50), but with two changes: Eq. (3) is used [rather than Eq. (36) of Ref. 30] and the time dependence is retained. The result is

$$i\hbar\frac{\partial}{\partial t}\Psi_k(\mathbf{r},t)=\bar{H}\Psi_k(\mathbf{r},t)-\sum_{k'} n_{k'}\int d^3r'\Psi^*_{k'}(\mathbf{r}',t)\Psi_k(\mathbf{r}',t)v(\mathbf{r}'-r)\Psi_{k'}(\mathbf{r},t) , \qquad (15)$$

$$\bar{H}=-\frac{\hbar^2}{2m}\nabla^2+\sum_l v_l(\mathbf{r}-\mathbf{R}_l)+\int d^3r' n(\mathbf{r}',t)v(\mathbf{r}'-\mathbf{r})+H_{\rm ext} , \qquad (16)$$

$$n(\mathbf{r},t)=\sum_k n_k\Psi^*_k(\mathbf{r},t)\Psi_k(\mathbf{r},t) , \qquad (17)$$

$$n_k\equiv\langle\hat{a}^\dagger_k\hat{a}_k\rangle . \qquad (18)$$

Since the expectation value (18) is to be evaluated in a time-independent Heisenberg state, n_k is constant. Up to this point the states k have not yet been specified. We can then require that they be defined in such a way that each state is exactly empty or filled by one electron at some time t_0 (e.g., in the remote past). It follows that

$$n_k=0 \text{ or } 1 \qquad (19)$$

at all times t. The Ψ_k are required to be orthonormal at t_0, with (15) enforcing this condition at all other times.

We now have the same simple picture as in a static self-consistent-field calculation: Only the "filled" states need be considered in the SCF equations (15)–(17), and one can imagine each electron as having its own state Ψ_k. Notice, however, that Ψ_k is an arbitrary time-dependent state, rather than an eigenstate of the Hamiltonian $H(t)$. The self-consistent potential must, of course, be updated as often as is necessary during a simulation. This should not be a major difficulty in simple cases—for example, when a single electron is promoted from a bonding to an antibonding state, changing the local charge density and potential.

In static calculations, it is conventional to replace the Hartree-Fock exchange term by a local potential $v_{\rm xc}(n(\mathbf{r}))$ representing exchange and correlation effects. In the same spirit, one can replace the last term of the time-dependent Hartree-Fock equation (15) by a potential $v_{\rm xc}(n(\mathbf{r},t))$ which is local in both space and time: $H=\bar{H}+v_{\rm xc}$. Let us separate H into a time-independent reference Hamiltonian H_0 and time-dependent perturbation

$$V(t)\equiv H(t)-H_0 . \qquad (20)$$

Substitution of (5) into (2) then yields the standard equation of motion in the interaction picture:[27]

$$i\hbar\frac{d}{dt}c_n(t)=\sum_m V_{nm}(t)c_m(t)\exp(i\omega_{nm}t)\ , \tag{21}$$

$$V_{nm}(t)\equiv\langle n|V(t)|m\rangle\ , \tag{22}$$

$$\omega_{nm}\equiv(\varepsilon_n-\varepsilon_m)/\hbar\ . \tag{23}$$

On a long time scale, the rapidly oscillating factor $\exp(i\omega_{nm}t)$ gives rise to energy conservation in time-dependent perturbation theory and Fermi's golden rule. However, (21) is exact on any time scale, and here this factor plays a somewhat different role: It may be integrated analytically over each time step Δt of a simulation. For example, suppose that $V(t)=\bar{V}(t)e^{-i\omega t}$, with $\bar{V}(t)$ a slowly varying function of time. If $\bar{V}$ is not too strong, (21) implies that $c_n(t)$ will also be slowly varying. Integration of (21) over one time step then gives

$$c_n(t_0+\Delta t)\approx c_n(t_0)-\sum_m \bar{V}_{nm}(t_0)c_m(t_0)\times e^{i\Delta\omega t_0}(e^{i\Delta\omega\Delta t}-1)/\hbar\Delta\omega\ , \tag{24}$$

$$\Delta\omega\equiv\omega_{nm}-\omega\ . \tag{25}$$

This result is relevant, e.g., to an electromagnetic field or plasma oscillation with $\hbar\omega\sim\hbar\omega_{nm}\sim1$ eV. On the other hand, a $V(t)$ associated with slow ionic motion corresponds to the special case $\omega=0$, and will be ineffective in producing transitions because of the rapid oscillations when $\omega_{nm}\neq0$.

During a simulation, the reference Hamiltonian may be updated as often as is necessary. Suppose that at time t we switch from H_0 with states $|n\rangle$ to H'_0 with states $|n'\rangle$. Then the two versions of (5) with $|n\rangle$, ε_n, and $|n'\rangle$, ε'_n can be set equal in order to obtain the coefficients

$$c'_n(t)=\sum_m c_m(t)e^{i(\varepsilon'_n-\varepsilon_m)t/\hbar}\langle n'|m\rangle\ . \tag{26}$$

Equation (21) thus provides a feasible numerical procedure for treating the electron dynamics. To calculate the forces on the ions, however, we need to adapt (14) to the TDSCF description. This can be achieved by writing $\mathcal{H}_{\text{ei}}$ in its second-quantized form

$$\mathcal{H}_{\text{ei}}=\int d^3r\,\hat{\Psi}^\dagger(\mathbf{r},t)\hat{\Psi}(\mathbf{r},t)\sum_l v_l(\mathbf{r}-\mathbf{R}_l)\ . \tag{27}$$

When (3) is substituted for $\hat{\Psi}$, the generalized Hellmann-Feynman theorem (14) is transformed into the TDSCF version (4) that was promised earlier.

The above formulation is suitable for first-principles calculations. In the simplest formulation for tight-binding calculations, we postulate a semiempirical Lagrangian

$$L=\sum_{l\alpha}\tfrac{1}{2}M_l\dot{X}_{l\alpha}^2-U_{\text{rep}}+\sum_k n_k\Psi_k^\dagger\cdot\left[i\hbar\mathbf{S}\frac{\partial}{\partial t}-\mathbf{H}\right]\cdot\Psi_k\ , \tag{28}$$

with the Hamiltonian matrix $\mathbf{H}$ and overlap matrix $\mathbf{S}$ assumed to depend only on the ion coordinates $X_{l\alpha}$ (and $\alpha=x,y,z$). We also require that the action $I=\int L\,dt$ be stationary with respect to variations $\delta X_{l\alpha}$, $\delta\Psi_k^*(a)$, and $\delta\Psi_k(a)$, obtaining

$$M\ddot{X}_{l\alpha}=-\sum_k n_k\Psi_k^\dagger\cdot\left[\frac{\partial\mathbf{H}}{\partial X_{l\alpha}}-i\hbar\frac{\partial\mathbf{S}}{\partial X_{l\alpha}}\frac{\partial}{\partial t}\right]\cdot\Psi_k-\frac{\partial U_{\text{rep}}}{\partial X_{l\alpha}}\ , \tag{29}$$

$$i\hbar\frac{\partial\Psi_k}{\partial t}=\mathbf{H}'\cdot\Psi_k\ ,\quad \mathbf{H}'\equiv\mathbf{S}^{-1}\cdot\mathbf{H}\ . \tag{30}$$

This time-dependent Schrödinger equation can again be solved using the interaction picture (5) and (21), and the ion motion can be calculated from the generalized Hellmann-Feynman theorem

$$M\ddot{X}=-\sum_k n_n\Psi_k^\dagger\cdot\left[\frac{\partial\mathbf{H}}{\partial X}-\frac{\partial\mathbf{S}}{\partial X}\cdot\mathbf{S}^{-1}\cdot\mathbf{H}\right]\cdot\Psi_k-\frac{\partial U_{\text{rep}}}{\partial X}\ , \tag{31}$$

where X is any ion coordinate. In an orthogonal tight-binding model, with $\mathbf{S}=\mathbf{1}$, the second term vanishes. Equation (31) is very similar to the Hellmann-Feynman theorem for ground-state tight-binding molecular dynamics.[8–10] The only difference is that the wave functions $\Psi_k(t)$ can correspond to electrons in excited states or undergoing transitions. This is, however, a very big difference, since excited-state chemistry is very different from ground-state chemistry.[31] For example, when an electron in a molecule is promoted from a bonding to an antibonding state, the interatomic forces can change from attractive to repulsive, and the molecule may dissociate. Absorption and stimulated emission of radiation can be included in a tight-binding simulation by adding a term H_{ext} to (30). In the dipole approximation,[27] H_{ext} involves matrix elements $\langle a|x|b\rangle$, and these can be treated as parameters like H_{ab} and S_{ab}.

A classical description of the radiation field and ion motion does not include spontaneous emission of photons and phonons. Perhaps one can also simulate the quantum fluctuations that give rise to spontaneous emission, by adding appropriate stochastic perturbations.

In summary, we have introduced a technique for simultaneously treating the dynamics of electrons and ions. There are actually three versions: The simplest assumes a tight-binding model, in which the electron Hamiltonian depends only on the ion positions and applied fields. Then our approach differs from ground-state tight-binding molecular dynamics[8–10] only in that the electrons are in excited states and undergoing transitions, and this is reflected in the generalized Hellmann-Feynman theorem (31). The next level is first-principles calculations with a ground-state Hamiltonian, but with the electrons in excited states. Finally, there is the level at which the Hamiltonian is computed self-consistently with the electrons in excited states. The present technique thus provides several choices for simulating the excited-state properties of molecules and materials.

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