Hellmann-Feynman theorem and the definition of forces in quantum time-dependent and transport problems

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The conventional Hellmann-Feynman theorem for the definition of forces on nuclei is not directly applicable to quantum time-dependent and transport problems. We present a rigorous derivation of a general Hellmann-Feynman-like theorem that applies to all quantum mechanical systems and reduces to well-known results for ground-state problems. It provides a rigorous definition of forces in time-dependent and transport problems. Explicit forms of Pulay-like forces are derived and the conditions for them to be zero are identified. A practical scheme for *ab initio* calculations of current-induced forces is described and the study of the transfer of a Si atom between two electrodes is presented as an example.

I. INTRODUCTION

The Hellmann-Feynman (HF) theorem[1] has been a key ingredient of the quantum mechanical treatment of forces acting on nuclei in molecules and solids. In turn, these forces are the key ingredient of *ab initio* calculations of atomic-scale structure and dynamics in materials physics, chemistry, and molecular biology.[2–8] In such calculations, the electron system is kept in its instantaneous ground state, for which the traditional formulations of the HF theorem apply. For example, for several decades, theoretical investigations of molecules and chemical reactions have relied on potential energy surfaces computed in this fashion. In the last two decades, a similar approach has been the basis for calculations in solids, e.g., surface reconstruction, phase transformations, defect configurations, and defect reactions. In more recent years, fully dynamical calculations (e.g., the Car-Parrinello method[2,3]) generally assume the electron system remains in its instantaneous ground state.

The conventional formulations of the HF theorem,[2–8] however, do not apply to two important classes of problems in which the electron system is not in the ground state. Both these classes are emerging frontiers for *ab initio* quantum mechanical calculations.

(a) Molecules and solids in *time-dependent* external fields, e.g., radiation. In such systems, the external field generally induces electronic excitations and nuclear motions. The advent of powerful free-electron lasers and of tabletop lasers that deliver intense ultrashort pulses has renewed interest in the photodissociation of molecules and other ultrafast reactions,[9] the generation of high harmonics, including x rays, from atoms in intense infrared pulses,[10,11] the photo-induced desorption of atoms and molecules from solid surfaces,[12] and other phenomena, especially in the nonlinear regime.

(b) *Transport* in nanostructures and molecules. The fabrication of electronic devices using nanoparticles or molecules[13,14] and the use of a scanning-tunneling microscope to create atomic-scale structures on crystal surfaces[15] represent transport problems for which the traditional Boltzmann equation approach does not apply.[16] Fully quantum mechanical calculations of transport properties are needed, including calculations of current-induced atomic rearrangements. The macroscopic manifestation of the latter, namely electromigration, has remained an open question through the years[17,18] and is ripe for direct first-principles calculations.

For both classes of problems, the conventional formulations of the HF theorem and its generalizations are not applicable and the proper definition of the force on nuclei has remained unsettled.[10,18–20] Some attempts to extend the HF theorem to nonstationary states have been proposed[22] but, as we show later in the paper, they rely on an incorrect physical assumption.

In this paper, we will first give a concise statement of the HF theorem for eigenstate and variational ground-state problems as a point of reference and identify the precise obstacles that have left the problem unsettled for the time-dependent and transport problems. We will then present a general form of the HF theorem that is applicable to all quantum mechanical systems with square-integrable wave functions. The proper definition of forces and their implementation in practical calculations will then become clear. We will show that this general theorem and its practical implementations reduce to the classic results for systems in the ground state. An example will be provided for the forces acting on a Si atom between two electrodes when steady-state current flows.

II. HF THEOREM FOR GROUND STATE

Throughout this paper we will present derivations using a many-body Hamiltonian H and many-body square-integrable wave functions Ψ for a system of nuclei and electrons without any particular approximations. Analogous derivations can easily be formulated using specific approaches to the many-body problem such as Hartree-Fock or density-

functional theory (DFT). The explicit equations for DFT are given in the Appendix.

Given the eigenvalue problem

$$H\Psi = E\Psi, \tag{1}$$

where H depends parametrically on a quantity λ and Ψ is square-integrable, it is straightforward to show by direct differentiation that

$$\frac{dE}{d\lambda} = \left\langle \Psi \left| \frac{\partial H}{\partial \lambda} \right| \Psi \right\rangle \Big/ \langle \Psi | \Psi \rangle + \left[\left\langle \Psi \left| H - E \right| \frac{\partial \Psi}{\partial \lambda} \right\rangle + \left\langle \frac{\partial \Psi}{\partial \lambda} \left| H - E \right| \Psi \right\rangle \right] \Big/ \langle \Psi | \Psi \rangle. \tag{2}$$

In view of Eq. (1), Eq. (2) reduces to

$$\frac{dE}{d\lambda} = \left\langle \Psi \left| \frac{\partial H}{\partial \lambda} \right| \Psi \right\rangle \Big/ \langle \Psi | \Psi \rangle. \tag{3}$$

This last equation represents the HF theorem for *exact* eigenstates. If the quantity λ is a given degree of freedom of the system, then the quantity $-dE/d\lambda$ given by Eq. (3) can be interpreted as the generalized force associated with it. In particular, if the nuclei (or ions) are treated as classical particles and λ is the position vector of a nucleus, then $-dE/d\lambda$ is the classical force on that nucleus.

The practical importance of the HF theorem is that energy derivatives are difficult to compute numerically, whereas the expression on the right in Eq. (3), the negative of which is known as the HF force, can be computed efficiently. However, it was recognized by early computational work using atom-centered basis functions that the HF force gave manifestly wrong results.[5] The origin of the problem is most succinctly illustrated by noting that, for a variational calculation of the ground-state energy E, when Ψ is expanded in terms of a *finite basis set*, one no longer has Eq. (1) but the more restrictive

$$\langle \Psi | H - E | \Psi \rangle = 0, \tag{4}$$

where E and Ψ now are the variational energy and wave function, respectively. Equation (4) is now a *matrix equation*. As a result, the second term in Eq. (2) is no longer zero.

Two approaches have been pursued in the literature:

(a) One requires that the basis set is such that the extra term in Eq. (2) is identically zero. This requirement, known as Hurley's condition,[21] is satisfied if the basis functions do not depend on λ (e.g., when the parameters λ are nuclear position vectors; such sets are known as ''floating sets'' in quantum chemistry; in solid state applications, the commonly used plane waves are such a set). The condition is also satisfied if the derivatives of the basis functions with respect to λ are themselves part of the basis set.[4] In such a case, the original HF theorem is satisfied. In order to prove these statements, one writes in matrix notation

$$\Psi = C\chi, \tag{5}$$

where $\{\chi\}$ is the basis set and C the expansion coefficients. From the stationarity principle, $\delta E/\delta\Psi = 0$, we get $\delta E/\delta C = 0$, so that only the derivatives $d\chi/d\lambda$ survive in $\partial\Psi/\partial\lambda$ in Eq. (2).

(b) One works with the full Eq. (2). The usual interpretation of this equation is that $-dE/d\lambda$ represents the exact force, the negative of the first term on the right is the HF force, and the negative of the last term is a correction term often referred to as the Pulay force.[5] This interpretation was backed by the fact that, as we already mentioned, attempts to use the HF force alone with atom-centered basis orbitals gave manifestly wrong results.[5] The Pulay force is routinely included in calculations using atom-centered basis functions and is in fact needed to produce realistic results. It is viewed as a correction to the HF force needed to make the calculation accurate to second order.[5,6]

From this perspective, it is clear why the problem of forces in time-dependent and transport problems remains unsolved: it is not obvious that, in these cases, one can meaningfully define a force in terms of an energy derivative. Moreover, it was recognized that there is no HF theorem that would connect the energy derivative to the practical HF force.[18] It has been argued, however, that, even in the absence of a HF theorem, the HF force [right-hand side of Eq. (3)] remains the correct quantum mechanical force for time-dependent and transport problems because of the Ehrenfest theorem that relates this force to the time derivative of the expectation value of the (generalized) momentum operator.[10,18] This assertion is appealing, but has not been tested and *runs contrary to the established fact* that, for variational ground-state calculations using atom-centered basis sets, the HF force alone is inadequate and the corrections introduced by the Pulay terms are not negligible.

III. TIME-DEPENDENT PROBLEM

We have now laid the groundwork to present a rigorous formulation of forces for all quantum mechanical problems. The first step is to recognize that the only correct and most general quantum mechanical definition of a force is the expectation value of the time derivative of the momentum operator.[23] For the most general, time-dependent quantum mechanical problem defined by

$$H\Phi = i\frac{\partial}{\partial t}\Phi \tag{6}$$

(we use units such that $\hbar = 1$ and we use Φ to denote time-dependent wave functions), the force for a given degree of freedom λ is defined by[23]

$$F = -i\frac{d}{dt}\left\langle \Phi \left| \frac{\partial}{\partial \lambda} \right| \Phi \right\rangle \Big/ \langle \Phi | \Phi \rangle. \tag{7}$$

If λ is the position vector of a given nucleus, then the force in Eq. (7) is simply the time derivative of the expectation value of the momentum operator of that nucleus.

If we specialize this definition to time-independent problems for which

$$\Phi(t) = e^{-iEt}\Psi, \tag{8}$$

we get immediately

$$F = -\frac{dE}{d\lambda}. \tag{9}$$

Two most important observations are in order: first, *the reduction of the force definition to the energy-derivative form is only possible for time-independent problems*; and second, for time-independent problems, this reduction is valid for both exact wave functions and wave functions expressed in terms of a finite basis set. These observations validate rigorously the long-standing assumption that, for time-independent eigenstate problems, the force can be defined in terms of the derivative of the energy. They also make clear the fact that, for time-dependent problems, the rigorous definition of the force is Eq. (7).

We now address the issue of connecting the rigorous force definition to the HF force in the general case. By direct differentiation of the definition (7) and use of Eq. (6), it is straightforward to show that, *for exact wave functions*

$$i\frac{d}{dt}\left\langle \Phi\left|\frac{\partial}{\partial\lambda}\right|\Phi\right\rangle=\left\langle \Phi\left|\frac{\partial H}{\partial\lambda}\right|\Phi\right\rangle. \tag{10}$$

This is the usual Ehrenfest theorem that can be found in textbooks.[23] In view of Eqs. (7) and (9), we see immediately that for time-independent problems, the Ehrenfest theorem reduces to Eq. (3), namely the HF theorem. In fact, the Ehrenfest theorem has been referred to as the time-dependent version of the HF theorem.[19] One observation is crucial, however. The Ehrenfest theorem [Eq. (10)] is only valid for *exact* wave functions. When the wave functions are expanded in terms of a finite basis set, as in most computational work, one must derive the corresponding *finite-set Ehrenfest-like theorem*. We note that, for finite basis sets, we no longer have Eq. (6), but the more restrictive

$$\left\langle \Phi\left|H-i\frac{\partial}{\partial t}\right|\Phi\right\rangle=0, \tag{11}$$

which is a matrix equation. By direct differentiation and some algebraic manipulation, we then get *the finite-set Ehrenfest theorem*:

$$i\frac{d}{dt}\left\langle \Phi\left|\frac{\partial}{\partial\lambda}\right|\Phi\right\rangle=\left\langle \Phi\left|\frac{\partial H}{\partial\lambda}\right|\Phi\right\rangle+\left\langle \frac{\partial\Phi}{\partial\lambda}\right|H-i\frac{\partial}{\partial t}\left|\Phi\right\rangle+\left\langle \Phi\left|H+i\frac{\partial}{\partial t}\right|\frac{\partial\Phi}{\partial\lambda}\right\rangle. \tag{12}$$

This is the central result of this paper and represents the most general form of an HF-like theorem that is applicable to all systems and allows a correct and unambiguous definition of forces for practical implementation. Note that this approximate form of the Ehrenfest theorem reduces to the exact form, Eq. (10), when the basis is complete, simply because Eq. (6) and its complex conjugate are then exact. When we specialize the finite-set theorem of Eq. (12) to the time-independent case, we immediately get Eq. (2). Thus, as is the case for time-independent problems, we find that when the appropriate form of the Ehrenfest theorem is used, the HF force is *not necessarily* the correct definition of force. The extra terms in Eq. (12) are the analog of the Pulay forces for the time-dependent problem. The Pulay forces can again be made zero by an appropriate choice of a basis set, as in the time-independent Hurley's condition. In other words, the Pulay forces are zero if the basis functions do not depend on λ or if their derivatives are also members of the set. In order to prove this statement, it is necessary to invoke the fact that in time-dependent problems, the action S defined by

$$S=\int_{t_0}^{t}\left\langle \Phi\left|H-i\frac{\partial}{\partial t}\right|\Phi\right\rangle dt \tag{13}$$

is stationary for a given Φ, namely $\delta S/\delta\Phi=0$, so that when we expand $\Phi=C\chi$, we have $\delta S/\delta C=0$. For plane waves and ''floating sets,'' the Pulay-like terms are again zero and the HF force is the exact force. Otherwise, the Pulay-like terms must be included. Note also that, in the most general case, stationarity of the action does not imply a minimum principle, indicating that the accuracy of the results is very sensitive to the choice of the approximate wave functions employed.[10]

We can now compare directly the above results with prior literature. As we already remarked, the assertion by Gross *et al.*[10] regarding the use of the HF force is rigorously correct in the limit of a complete basis set and remains valid when the generalized Hurley condition is satisfied, as discussed previously (see also the Appendix). Otherwise, Pulay-like forces must be included. It is also clear from the above analysis why the Bala *et al.* results[22] are not correct: the correct definition of the force in quantum mechanics is the time derivative of the expectation value of the momentum operator and *not* the λ derivative of the expectation value of the Hamiltonian on time-dependent wave functions.

IV. STEADY-STATE TRANSPORT PROBLEM

We turn now to the transport problem. The general formalism above is actually valid for all problems describable by square-integrable wave functions. The only question, therefore, is one of normalization of wave functions. In the eigenstate and variational ground-state problems one deals with either finite systems (molecules, clusters) or with infinite solids for which square-integrability is attained through periodic Born–von Kármán boundary conditions. For transport problems, square-integrability is ensured if one describes the complete circuit, including, e.g., the battery or generator. In the most general case of time-dependent power source, the above time-dependent formalism is completely valid. For practical calculations, however, one normally treats a system, say a device D, in contact with electrodes that act as reservoirs of electrons and serve merely as boundary conditions for the wave function of D. Square integrability can then be assured by constructing new many-electron wave functions from wave packets centered at individual one-electron energies.

For time-independent direct-current (dc) *steady-state* transport, the most general form of the many-body wave function of the system D is again as in Eq. (8), where now E is a phase factor with units of energy. Using this form in Eq. (13) we find that the action becomes

$$S=\langle\Phi|H-E|\Phi\rangle(t-t_0). \tag{14}$$

The stationarity of the action[10] now yields

$$\delta\langle\Phi|H-E|\Phi\rangle=0. \tag{15}$$

The equation above shows that the dc transport problem can be rigorously mapped onto a variational problem where $\langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle$ is the steady-state energy of the system.

It differs from the ground-state problem only in the form of boundary conditions (closed versus open). Again, for plane waves and ''floating sets,'' the HF force represents the total force whereas for other sets Pulay-like forces must be included as in Eq. (2).

So far our derivations were carried out for the many-body Hamiltonian H and wave functions Ψ or Φ. For practical implementations, one normally separates the nuclear and electronic degrees of freedom and treats the nuclei as classical particles (see the Appendix). The Hamiltonian then depends parametrically on the nuclear position vectors, which can be treated as λ's in the present theory. The corresponding forces are the classical forces on the nuclei. For ground-state and time-dependent problems the general theory above can then easily be cast within the respective Hartree-Fock or density-functional formulations of the many-electron problem. For dc transport, Eq. (15) allows us to conclude that ground-state density-functional theory is again applicable with the steady-state energy of the system D playing the role of the ground-state energy. This result provides formal justification for the use of one-electron theories for transport calculations. We note, however, that for the transport problem, a practical implementation is still lacking for realistic systems. We conclude the paper by summarizing the main elements of such a practical scheme.

We consider the system D and two (or more) electrodes (R and L for right and left). Each of these systems can be treated separately by density functional theory. Let us designate the corresponding *single-particle* Hamiltonians by H_D, H_R, and H_L. The coupling between the system and the electrodes can then be included by defining the total single-particle Hamiltonian as

$$H=H_D+H_L+H_R+H_{LC}^I+H_{RC}^I, \tag{16}$$

where H_{LC}^I and H_{RC}^I are Hermitian operators to be determined. Only the Hamiltonians H_{LC}^I, H_{RC}^I, and H_D are assumed to depend on the position of the atoms. The external electric field is introduced by requiring that, far from the system, the Fermi-level difference between the left and right electrodes is equal to the desired value.[20] As we showed above, the steady-state energy of the system is defined in terms of the ground-state energy functional evaluated with the new wave functions obeying the transport boundary conditions.[24]

The most effective approach to a self-consistent determination of H_{LC}^I, H_{RC}^I, and Ψ is the Green's function method, where $H_{LC}^I+H_{RC}^I+H_D$ is viewed as the perturbation to the bare electrodes. So far this problem has been addressed *without considering the problem of forces by several authors*.[20,25,26] A practical scheme has been developed by Lang[20] by assuming that the electrodes are described by ''jellium,'' namely, a homogeneous electron gas with a smeared-out compensating positive background. Formulations using real metals are *not* well-suited for practical calculations because of ambiguities in ordering the wave functions by energy.[26] We propose, therefore, the following scheme for practical calculations, including force calculations: The electrodes can be approximated by jellium only far from the system-electrode junctions so that the electrode wave functions can be easily ordered by the asymptotic behavior as plane waves. We anticipate that only a few layers of metal atoms would be needed attached to jellium continua. For the actual calculations, the metal layers are viewed as part of the system in the cavity between jellium electrodes. Lang's formalism can then be used to determine H and Ψ self-consistently, and current-induced forces on atoms can be computed as in variational problems in accordance with the theorem proven in the present paper.[27] The spurious resistance introduced by the jellium-metal interface can be calculated separately and subtracted. We note that the discrete as well as the continuous spectrum of the whole system can be included in the formalism above in a straightforward way. This is of extreme importance in such phenomena such as electromigration, where the contributions coming from the continuous and discrete parts of the spectrum are of the same order of magnitude.[18]

We conclude with a practical example applying the formulation above to the problem of a Si atom between two electrodes.[28] The two electrodes are kept at a distance of 4.5 Å. An external bias is applied between the right and left electrode, the left electrode being positive with respect to the right electrode. The spectrum of the present system has a discrete and a continuum component. For the single-particle wave functions in the discrete part of the spectrum ψ_i, square-integrability is satisfied because the ψ_i's are localized. For each energy in the continuum we build square-integrable wave functions $\tilde{\psi}$ in an energy region Δ, as we stated above:

$$\tilde{\psi}=A\int_\Delta dE\,\psi, \tag{17}$$

where A is a normalization constant and ψ's are single-particle wave functions in the continuum. As in Ref. 29 we choose plane waves to represent the Hilbert space.[30] According to Eq. (2), the Pulay-like terms are thus identically zero. The force $\mathbf{F}$ acting on the atom at position $\mathbf{R}$ due to the electron distribution as modified by the external bias is thus

$$\mathbf{F}=\sum_i \left\langle \psi_i\left|\frac{\partial H}{\partial \mathbf{R}}\right|\psi_i\right\rangle+\lim_{\Delta\to 0}\int_\sigma dE\left\langle\tilde{\psi}\left|\frac{\partial H}{\partial \mathbf{R}}\right|\tilde{\psi}\right\rangle. \tag{18}$$

The sum and integral in Eq. (18) include spin variable too. In the present case, no ion-ion interaction must be included. The continuum integration σ covers the part of the spectrum occupied by the electrons at a given bias: at $T=0$, from the bottom of the conduction band on the left to the quasi-Fermi-level on the right.[31]

In the case at hand, the force is directed along the direction perpendicular to the electrode surfaces. The results are plotted in Fig. 1 for two different external bias conditions: 0 V and 3 V.[28] At zero bias the Si atom has two stable and one metastable configurations. The stable configurations correspond to the atom at about 1.2 Å from the two metals. The metastable configuration corresponds to the atom between the two electrodes. The stable configurations at zero bias coincide exactly with the equilibrium positions obtainable from standard density-functional total-energy calculations.[32]

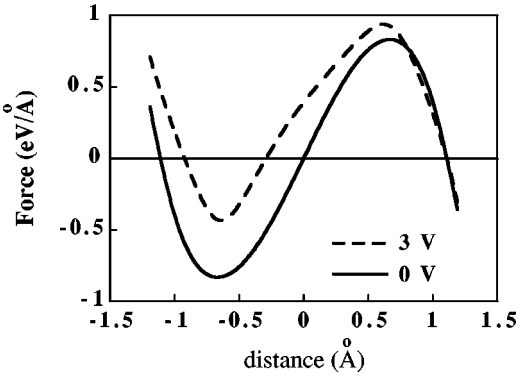

FIG. 1. Force on a single Si atom between two electrodes separated by 4.5 Å for two different external biases: 0 V and 3 V. Positive force pushes the atom to the right. Zero distance corresponds to the atom between the two electrodes.

The work necessary to bring the atom from one electrode to the other can be calculated from the curves in Fig. 1 as the integral between the metastable and stable configurations. At zero bias the work done is about 0.5 eV. Applying 3 V across the electrodes (the left electrode is at the higher bias), the stable positions shift slightly towards the right electrode due to a transfer of charge on the left electrode. Finally, the activation barrier to bring the atom from its left stable configuration to the new metastable position decreases to about 0.1 eV. The atom is essentially free to jump to the right electrode when the bias is 3 V.

V. CONCLUSIONS

We presented a general HF theorem that applies to all quantum mechanical systems and allows a rigorous definition of forces in all cases, including those where a finite basis set is used to represent the system wave functions. In the latter case, Pulay-like forces arise that can be set to zero with a particular choice of the basis functions. We also presented a practical scheme for transport calculations in nanostructures that includes current-induced forces on atoms. The latter scheme is particularly important nowadays to provide valuable insight into current effects on molecular devices.

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APPENDIX: FORCES IN DFT

We explicitly write in this appendix the expressions of the HF forces in DFT. We recall that the total energy of a many-electron system with charge density $n(\mathbf{r})$ in an external potential $V(\mathbf{r})$ can be written as a functional of the density[33]

$$E[n]=T_s[n]+\int V(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \frac{e^2}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+E_{\mathrm{xc}}[n]. \quad \text{(A1)}$$

T_s is the kinetic energy of noninteracting electrons, and $E_{\mathrm{xc}}[n]$ is the exchange-correlation energy. The quantum mechanical problem is solved with variational wave functions. According to Eq. (3), the electronic contribution to the force acting on a nuclear degree of freedom λ is thus

$$F=-\frac{dE[n]}{d\lambda}=-\int\frac{\partial V(\mathbf{r})}{\partial\lambda}n(\mathbf{r})d\mathbf{r}-\int\frac{\delta E(\mathbf{r})}{\delta n}\frac{\partial n(\mathbf{r})}{\partial\lambda}d\mathbf{r}, \quad \text{(A2)}$$

where $\delta E(\mathbf{r})/\delta n$ is the variation of the functional with respect to the density. The first term in Eq. (A2) is the HF force, while the second is the Pulay-like term. If the ionic potentials are spherically symmetric and their non-Coulomb parts do not overlap, a classical electrostatic term, representing the ion-ion interaction, must be added to Eq. (A2) to obtain the total force on nuclei.

In time-dependent DFT, Eq. (6) decouples into a set of coupled equations for all electrons ψ_i and nuclei ϕ_i (with charge Z_i) under external time-dependent potentials $V(\mathbf{r},t)$ and $V(\lambda,t)$, respectively,

$$i\frac{\partial}{\partial t}\psi_i(\mathbf{r},t)=\left(T_s[n]+V(\mathbf{r},t)+\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+E_{\mathrm{xc}}[n]\right)\psi_i(\mathbf{r},t), \quad \text{(A3)}$$

$$i\frac{\partial}{\partial t}\phi_i(\lambda,t)=\left[T_\lambda+V(\lambda,t)-Z_i\times\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+E_{\mathrm{xc}}[n](\lambda,t)\right]\phi_i(\lambda,t),$$

where T_λ is the nuclei kinetic energy and $E_{\mathrm{xc}}[n](\lambda,t)$ is the nuclear exchange-correlation potential. Note that, in our notation, $V(\mathbf{r},t)$ and $V(\lambda,t)$ contain the electron-ion and ion-ion interactions, respectively. Assuming the nuclei as classical particles with nuclear distribution $n_i(\lambda,t)=|\phi_i(\lambda,t)|^2=\delta(\lambda-\lambda_i(t))$ and applying Eq. (12) to the nuclear motion, the force on the nuclei is

$$F_i(t)=-\nabla_{\lambda_i(t)}V(\lambda,t)-Z_i\times\int\frac{n(\mathbf{r}')}{|\lambda_i(t)-r'|^2}+Z_i\int\frac{\nabla_{\lambda_i(t)}n(\mathbf{r}')}{|\lambda_i(t)-r'|}. \quad \text{(A4)}$$

The last term of Eq. (A4) is the Pulay-like force in time-dependent DFT.

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