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Error cancellation in the molecular dynamics method for total energy calculations

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Abstract. A detailed analysis of Car and Parrinello's molecular dynamics method is presented. It is shown that the degrees of freedom associated with the electronic wavefunctions do not behave as classical degrees of freedom because their motions are damped by the constraint of normalisation of the wavefunctions. Therefore, the accuracy to which the electronic configuration remains on the Born–Oppenheimer surface and the ionic configuration evolves at constant energy during a dynamical simulation is not a result of treating the electronic degrees of freedom as classical degrees of freedom. Instead it is shown that the accuracy of the constant energy evolution of the ionic system in a molecular dynamics calculation is explained by the tendency for errors in the Hellmann–Feynman forces to cancel when the molecular dynamics equations of motion are used to evolve the electronic degrees of freedom. A quantitative analysis of this error cancellation is presented. By analysing the magnitude of the error in the electronic wavefunction, a criterion is developed for the maximum velocity of propagation of the ions at which the evolution of the electronic configuration remains stable.

1. Introduction

The molecular dynamics method developed by Car and Parrinello (1985) has produced an enormous increase in the power of the total energy pseudopotential technique (for details of the total energy pseudopotential technique see Ihm *et al* 1979). Dynamical simulations of ionic systems can be performed in which the electronic configuration is relaxed to its groundstate using the molecular dynamics method and the forces on the ions are calculated using the Hellmann–Feynman theorem (Hellmann 1937, Feynman 1939). One of the remarkable things about the molecular dynamics method is the ability to perform dynamical simulations of the ionic configuration for several thousand timesteps with a negligible loss of energy from the ionic system (Hohl *et al* 1987, Car and Parrinello 1988, Ballone *et al* 1988), which would appear to require that the Hellmann–Feynman forces are correct to an extremely high accuracy. Hellmann–Feynman forces are notoriously sensitive to errors in the electronic wavefunction; the errors in the Hellmann–Feynman forces are first order with respect to the error in the wavefunction so that the accuracy in the Hellmann–Feynman forces can only be achieved if the electronic configuration is the instantaneous groundstate configuration to the same accuracy. The ionic configuration is constantly evolving in a dynamical simulation and it is almost inconceivable that the electronic configuration remains this close to the instantaneous groundstate during the entire simulation. It has been suggested that the accuracy of the ionic trajectories is a result of using molecular dynamics equations of

motion to evolve both the ionic and electronic degrees of freedom. This appears to imply that the electronic and ionic degrees of freedom are in thermal equilibrium. In § 2 it will be shown that this is definitely not the case. The electronic degrees of freedom do not behave like classical degrees of freedom; the motions of the electronic states are continuously damped by the constraint of normalisation even when there is no damping explicitly applied in the molecular dynamics equations of motion for these degrees of freedom. In § 3 the evolution of the electronic degrees of freedom is investigated in greater detail. It is shown that during a dynamical simulation of the ionic system energy is continually supplied to the electronic degrees of freedom and then removed by the damping due to the constraint of normalisation. The accuracy of the constant energy evolution of the ionic system is critically dependent on the damping of the electronic degrees of freedom. If the electronic degrees of freedom were undamped the energy of the ionic system would not be constant during a dynamical simulation: the electronic degrees of freedom would act as a thermal reservoir for the ionic system and the energy of each ion would fluctuate according to a Boltzmann distribution. In § 4 it is shown that the accuracy of the ionic trajectories is explained by a tendency for the errors in the Hellmann–Feynman forces to cancel when the molecular dynamics equations of motion are used to evolve the electronic configuration. This error cancellation makes the loss of energy from the ionic system second order with respect to the error in the electronic wavefunction. In § 5 the stability of the evolution of the electronic configuration is considered and it is shown that the velocity of the ions must be restricted if the electronic configuration is to evolve stably.

2. Evolution of the electronic degrees of freedom

In the molecular dynamics formulation the electronic wavefunctions are treated as dynamical variables and a kinetic energy term appears in the Lagrangian for each of these degrees of freedom. In a dynamical simulation of the ionic system the ionic degrees of freedom are also included as dynamical variables in the Lagrangian and the molecular dynamics Lagrangian is written as follows:

$$\mathcal{L} = \sum_i \frac{1}{2} \mu \int dr^3 |\dot{\psi}_i|^2 + \sum_I \frac{1}{2} M_I |\dot{\mathbf{R}}_I|^2 - E[\{\psi_i\}, \{\mathbf{R}_I\}] \quad (1)$$

where ψ_i are the electronic states, μ is a fictitious mass associated with the dynamics of the electronic states, M_I is the mass of ion I and \mathbf{R}_I is its position, and E is the Kohn–Sham energy functional (Kohn and Sham 1965). The fictitious mass associated with the dynamics of the electronic states μ will be set equal to unity from now on and the electronic configuration will be represented by a many-particle wavefunction ψ which in the case of a density functional calculation is a simple product of single-particle wavefunctions.

The molecular dynamics Lagrangian gives the following equation of motion for the electronic wavefunction

$$\ddot{\psi} = -(H - \lambda)\psi \quad (2)$$

where H is the Kohn–Sham Hamiltonian and λ is essentially just an energy shift that is normally taken to be equal to the expectation value of the energy of state ψ .

If ψ is expanded in the basis set of the eigenstates of Hamiltonian H

$$\psi = \sum_n c_n \varphi_n \quad (3)$$

and (3) is substituted into (2), the following equation of motion for the coefficient of the basis state φ_n is obtained:

$$\ddot{c}_n = -(\varepsilon_n - \lambda)c_n \quad (4)$$

where ε_n is the eigenvalue of φ_n .

Integrating these equations of motion assuming that the velocities of the coefficients are zero initially gives the coefficients at time t as

$$c_n(t) = \cos[(\varepsilon_n - \lambda)^{1/2}t]c_n(0) \quad \varepsilon_n > \lambda \quad (5)$$

$$c_n(t) = \cosh[|\varepsilon_n - \lambda|^{1/2}t]c_n(0) \quad \varepsilon_n < \lambda \quad (6)$$

where $c_n(0)$ is the value of the coefficient initially.

It can be seen that the amplitudes of the coefficients of the eigenstates of H which have energies greater than λ oscillate with time, while the amplitudes of the coefficients of the eigenstates with energies less than λ increase with time so that the total magnitude of ψ under the unconstrained molecular dynamics equations of motion increases with time provided that the value of λ is larger than the ground-state energy of H and that ψ spans the ground state. Under the unconstrained dynamics the magnitude of ψ will only remain constant in time if the energy shift λ is chosen to be less than the ground-state energy. Such a choice for λ would never allow the system to reach a global energy minimum and Hellmann–Feynman forces could not be calculated because ψ would never be an eigenstate of the Hamiltonian. Therefore the value of λ must be chosen to be larger than the ground-state energy for a molecular dynamics calculation to be successful. Under the constrained dynamics the electronic wavefunction must remain normalised and if λ is larger than the ground-state eigenvalue normalising the wavefunction will reduce the magnitudes and the velocities of the coefficients c_n . This reduces the kinetic energy in the electronic degrees of freedom and thus damps the motions of the electronic degrees of freedom even when there is no damping explicitly applied in the molecular dynamics equations of motion. The removal of the excess energy from the electronic degrees of freedom eventually forces the electronic configuration to converge to the groundstate. In the following section it will be shown that the removal of the kinetic energy from the electronic degrees of freedom is necessary if the ionic system is to evolve at constant energy during a dynamical simulation.

3. Evolution of electronic and ionic degrees of freedom

If all the degrees of freedom in the molecular dynamics Lagrangian behaved as classical degrees of freedom the total energy associated with all the degrees of freedom in the Lagrangian would be constant because the Lagrangian is independent of time so that

$$\sum_i \frac{1}{2}\mu \int dr^3 |\dot{\psi}_i|^2 + \sum_I \frac{1}{2}M_I |\dot{\mathbf{R}}_I|^2 + E[\{\psi_i\}, \{\mathbf{R}_I\}] = \text{constant}. \quad (7)$$

If the motions of the ions are to be correctly described during a dynamical simulation the total energy in the ionic system should be constant, which requires that

$$\sum_I \frac{1}{2}M_I |\dot{\mathbf{R}}_I|^2 + E[\{\psi_i\}, \{\mathbf{R}_I\}] = \text{constant}'. \quad (8)$$

Equations (7) and (8) imply that the kinetic energy of the electronic degrees of freedom must be constant if the total energy in the ionic system is to remain constant.

However, if the electronic configuration was at rest in its ground state before the ions started to move then the kinetic energy in the electronic degrees of freedom would be zero initially and according to (7) and (8) the electronic configuration cannot evolve to its new groundstate. In the previous section it was shown that the normalisation of the wavefunctions damps the motion of the electronic degrees of freedom so that (7) is actually not constant but instead decreases with time due to the damping of the electronic degrees of freedom. This provides a mechanism for removing kinetic energy from the electronic degrees of freedom but it cannot provide the kinetic energy needed for the electronic configuration to evolve to its new ground state. From (7) and (8) it would appear that the electronic configuration can only relax to its new ground state by removing energy from the ionic system. This would lead to a very large damping of the ionic motions and this is not observed in molecular dynamics calculations. If the ionic configuration is to evolve at constant energy the kinetic energy required for the electronic degrees of freedom to evolve to the new ground state must be provided from a different source. The source of this energy will now be investigated.

For an accurate description of the ionic trajectories the forces on the ions should be calculated only when the electronic configuration is in the instantaneous ground-state configuration. The forces are assumed to vary slowly along the paths of the ions and the change in the potential energy in the ionic system due to moving the ions is taken to be

$$\sum_I \left\langle \varphi_0 \left| \frac{\partial H(\{\mathbf{R}_I\})}{\partial \mathbf{R}_I} \right| \varphi_0 \right\rangle \cdot \Delta \mathbf{R}_I = - \sum_I \mathbf{f}_I \cdot \Delta \mathbf{R}_I \quad (9)$$

where H is the Hamiltonian, φ_0 is the instantaneous ground-state wavefunction at the beginning of the time step, \mathbf{f}_I is the force on ion I at the beginning of the time step and $\Delta \mathbf{R}_I$ is the distance move by ion I . It will be assumed that the Coulomb energy of the ionic system is included in the Hamiltonian so that the derivative of the Hamiltonian with respect to the position of the ion includes the force exerted on the ion due to the Coulomb interaction with the other ions in the system.

If the forces on the ions were calculated when the ions have reached their new positions before the electronic configuration is allowed to evolve to the new ground-state configuration it would be found that the forces on the ions had changed significantly from their initial values. The extra work involved in moving the ions against the forces generated by the fixed electronic configuration is ignored in molecular dynamics calculations but it is this work that provides the energy for the electronic configuration to evolve to the new ground-state configuration. This extra work appears in the energy of the electronic system as an excitation of the electronic configuration from its ground state.

The work done moving the ions when the electronic configuration is kept fixed is equal to

$$\sum_I \int_{\mathbf{R}_I^1}^{\mathbf{R}_I^2} \left\langle \varphi_0 \left| \frac{\partial H(\mathbf{R} = \mathbf{R}_I)}{\partial \mathbf{R}} \right| \varphi_0 \right\rangle \cdot d\mathbf{R}_I = - \sum_I \int_{\mathbf{R}_I^1}^{\mathbf{R}_I^2} \mathbf{f}'_I \cdot d\mathbf{R}_I \quad (10)$$

where \mathbf{R}_I^1 is the position of ion I at the beginning of the time step, \mathbf{R}_I^2 is its position at the end of the time step and \mathbf{f}'_I is the instantaneous force on the ion. If this expression for the work done by the ion is computed and included in (7), the total energy associated with the molecular dynamics Lagrangian would remain constant during the displacement of the ions although damping of the electronic degrees of freedom by the constraint of normalisation would subsequently remove energy from the system. If the dynamics of the ions was generated from (10) energy would be transferred from the ionic system to

the electronic system and this would lead to a rapid damping of the motions of the ions and produce a totally fictitious dynamics for the ionic system. A correct description of the ionic dynamics is generated if (8) is constant and this requires that the forces on the ions are only calculated when the electronic configuration is in the ground state of the instantaneous ionic configuration. It will now be shown that the difference between the two values of the work done by the ions appears in the electronic degrees of freedom as an excitation of electronic configuration from its new ground state.

The Hamiltonians for the ions in their instantaneous positions at the beginning and end of the time step will be written as $H(\{\mathbf{R}_I^1\})$ and $H(\{\mathbf{R}_I^2\})$. The eigenstates of these Hamiltonians are given by

$$H(\{\mathbf{R}_I^1\})\varphi_n = \lambda_n\varphi_n \quad (11)$$

$$H(\{\mathbf{R}_I^2\})\chi_n = \varepsilon_n\chi_n, \quad (12)$$

where each eigenstate is a many-particle eigenstate which in the case of a density functional calculation is a product of Kohn–Sham eigenstates.

Hamiltonians $H(\{\mathbf{R}_I^1\})$ and $H(\{\mathbf{R}_I^2\})$ are related by

$$H(\{\mathbf{R}_I^2\}) = H(\{\mathbf{R}_I^1\}) + \sum_I \Delta\mathbf{R}_I \cdot \nabla_I [v_I(\mathbf{r} - \mathbf{R}_I^1)] + \Delta V_{\text{el}} \quad (13)$$

$$H(\{\mathbf{R}_I^2\}) = H(\{\mathbf{R}_I^1\}) + \Delta V_{\text{ion}} + \Delta V_{\text{el}}, \quad (14)$$

where $\Delta\mathbf{R}_I = \mathbf{R}_I^2 - \mathbf{R}_I^1$, $v_I(\mathbf{r})$ is the ionic pseudopotential for ion I and ΔV_{el} is the change in the self-consistent electronic potential on displacing the ions from positions \mathbf{R}_I^1 to \mathbf{R}_I^2 .

The electronic configuration at the beginning of the time step is in the ground state of Hamiltonian $H(\{\mathbf{R}_I^1\})$ and it remains in this state as the atoms are moved by $\Delta\mathbf{R}_I$. The Hellmann–Feynman forces on the atoms in positions \mathbf{R}_I^1 are

$$\mathbf{f}_I^1 = -\langle\varphi_0|\nabla_I v_I(\mathbf{r} - \mathbf{R}_I^1)|\varphi_0\rangle + \mathbf{F}_I^1, \quad (15)$$

where \mathbf{F}_I^1 is the force exerted on ion I in position \mathbf{R}_I^1 due to the Coulomb interaction with the other ions in the system.

The forces on the atoms in positions \mathbf{R}_I^2 before relaxing the electronic configuration are

$$\mathbf{f}_I^2 = -\langle\varphi_0|\nabla_I v_I(\mathbf{r} - \mathbf{R}_I^2)|\varphi_0\rangle + \mathbf{F}_I^2. \quad (16)$$

After relaxing the electronic configuration to the ground state for the ions in positions \mathbf{R}_I^2 the forces on the ions are given by

$$\mathbf{f}_I^2 = -\langle\chi_0|\nabla_I v_I(\mathbf{r} - \mathbf{R}_I^2)|\chi_0\rangle + \mathbf{F}_I^2. \quad (17)$$

If the Hellmann–Feynman forces are calculated with the electrons in the instantaneous ground-state configuration as the ions move between \mathbf{R}_I^1 and \mathbf{R}_I^2 the work done by the ions is equal to

$$-\sum_I \frac{1}{2}(\mathbf{f}_I^1 + \mathbf{f}_I^2) \cdot \Delta\mathbf{R}_I \quad (18)$$

but if the electronic configuration remains in state φ_0 the work done moving the ions against the fixed electronic configuration is equal to

$$-\sum_I \frac{1}{2}(\mathbf{f}_I^1 + \mathbf{f}_I^{2'}) \cdot \Delta\mathbf{R}_I. \quad (19)$$

Expressing φ_0 in terms of the basis set $\{\chi\}$ to first order in perturbation theory gives

$$\varphi_0 = \frac{1}{Z} \left(\chi_0 - \sum_{n \neq 0} \frac{\langle \chi_n | \Delta V_{sc} | \chi_0 \rangle}{\epsilon_0 - \epsilon_n} \chi_n \right) \quad (20)$$

where $\Delta V_{sc} = \Delta V_{ion} + \Delta V_{ei}$ is the change in the total self-consistent potential on moving the ions from positions \mathbf{R}_I^1 to \mathbf{R}_I^2 . Z is a normalisation constant given by

$$Z^2 = 1 + \sum_{n \neq 0} \left| \frac{\langle \chi_n | \Delta V_{sc} | \chi_0 \rangle}{\epsilon_0 - \epsilon_n} \right|^2. \quad (21)$$

The difference between the two values for the work done by the ions is

$$- \sum_I \frac{1}{2} (f_I^{2'} - f_I^2) \cdot \Delta \mathbf{R}_I \quad (22)$$

which is equal to

$$\frac{1}{2} [\langle \varphi_0 | \Delta V_{ion} | \varphi_0 \rangle - \langle \chi_0 | \Delta V_{ion} | \chi_0 \rangle]. \quad (23)$$

Substituting for φ_0 from (20) in (23) gives

$$\frac{1}{2} \left[\frac{1}{Z^2} \left(\left\langle \chi_0 - \sum_{n \neq 0} \frac{\langle \chi_0 | \Delta V_{sc} | \chi_n \rangle}{\epsilon_0 - \epsilon_n} \chi_n | \Delta V_{ion} | \chi_0 - \sum_{n \neq 0} \frac{\langle \chi_n | \Delta V_{sc} | \chi_0 \rangle}{\epsilon_0 - \epsilon_n} \chi_n \right\rangle \right) - \langle \chi_0 | \Delta V_{ion} | \chi_0 \rangle \right]. \quad (24)$$

To second order in the potentials ΔV_{sc} and ΔV_{ion} the difference between the two values of the work done on moving the ions is

$$- \sum_{n \neq 0} \frac{\text{Re}(\langle \chi_0 | \Delta V_{sc} | \chi_n \rangle \langle \chi_n | \Delta V_{ion} | \chi_0 \rangle)}{\epsilon_0 - \epsilon_n}. \quad (25)$$

The excitation energy in the electronic system after displacing the ions to positions \mathbf{R}_I^2 with the electronic configuration fixed in state φ_0 is

$$\langle \varphi_0 | H(\{\mathbf{R}_I^2\}) - \frac{1}{2} \Delta V_{ei} | \varphi_0 \rangle - \langle \chi_0 | H(\{\mathbf{r}_I^2\}) | \chi_0 \rangle. \quad (26)$$

The factor of $\frac{1}{2}$ multiplying ΔV_{ei} is a self-energy correction which is required because ΔV_{ei} is first order with respect to the change in the wavefunction. Substituting for φ_0 from (20) in (26) gives

$$\frac{1}{Z^2} \left\langle \chi_0 - \sum_{n \neq 0} \frac{\langle \chi_0 | \Delta V_{sc} | \chi_n \rangle}{\epsilon_0 - \epsilon_n} \chi_n | H(\{\mathbf{R}_I^2\}) - \frac{1}{2} \Delta V_{ei} | \chi_0 - \sum_{n \neq 0} \frac{\langle \chi_n | \Delta V_{sc} | \chi_0 \rangle}{\epsilon_0 - \epsilon_n} \chi_n \right\rangle - \langle \chi_0 | H(\{\mathbf{R}_I^2\}) | \chi_0 \rangle \quad (27)$$

This is

$$\frac{1}{Z^2} \left(\epsilon_0 - \sum_{n \neq 0} \epsilon_n \left| \frac{\langle \chi_0 | \Delta V_{sc} | \chi_n \rangle}{\epsilon_0 - \epsilon_n} \right|^2 - \frac{1}{2} \langle \chi_0 | \Delta V_{ei} | \chi_0 \rangle + \sum_{n \neq 0} \frac{\text{Re}(\langle \chi_0 | \Delta V_{sc} | \chi_n \rangle \langle \chi_n | \Delta V_{ei} | \chi_0 \rangle)}{\epsilon_0 - \epsilon_n} \right) - \epsilon_0. \quad (28)$$

Expanding $1/Z^2$ to second order in ΔV_{sc} and retaining terms to second order gives

$$\epsilon_0 \left[1 - \sum_{n \neq 0} \left| \frac{\langle \chi_0 | \Delta V_{sc} | \chi_n \rangle}{\epsilon_0 - \epsilon_n} \right|^2 \right] + \sum_{n \neq 0} \epsilon_n \left| \frac{\langle \chi_0 | \Delta V_{sc} | \chi_n \rangle}{\epsilon_0 - \epsilon_n} \right|^2$$

$$-\frac{1}{2}\langle\chi_0|\Delta V_{\text{el}}|\chi_0\rangle + \sum_{n\neq 0} \frac{\text{Re}[\langle\chi_0|\Delta V_{\text{sc}}|\chi_n\rangle\langle\chi_n|\Delta V_{\text{el}}|\chi_0\rangle]}{\varepsilon_0 - \varepsilon_n} - \varepsilon_0. \quad (29)$$

The expectation value $\langle\chi|H(\{\mathbf{R}_I^2\})|\chi\rangle$ is quadratic with respect to all variations of χ from χ_0 . ΔV_{el} is first order with respect to variations in χ from χ_0 so by the variational principle the term $\langle\chi_0|\Delta V_{\text{el}}|\chi_0\rangle$ in (29) is zero.

To second order in ΔV_{sc} and ΔV_{el} , the excitation energy in the electronic system after displacing the ions from positions \mathbf{R}_I^1 to \mathbf{R}_I^2 is

$$\sum_{n\neq 0} -\frac{\text{Re}[\langle\chi_0|\Delta V_{\text{sc}}|\chi_n\rangle\langle\chi_n|\Delta V_{\text{sc}}|\chi_0\rangle]}{\varepsilon_0 - \varepsilon_n} + \sum_{n\neq 0} \frac{\text{Re}[\langle\chi_0|\Delta V_{\text{sc}}|\chi_n\rangle\langle\chi_n|\Delta V_{\text{el}}|\chi_0\rangle]}{\varepsilon_0 - \varepsilon_n} \quad (30)$$

or

$$\sum_{n\neq 0} -\frac{\text{Re}[\langle\chi_0|\Delta V_{\text{sc}}|\chi_n\rangle\langle\chi_n|\Delta V_{\text{ion}}|\chi_0\rangle]}{\varepsilon_0 - \varepsilon_n} \quad (31)$$

which is equal to the difference between the two values for the work done by the ions (25). Therefore, the difference between the two values for the work done by the ions appears in the Kohn–Sham energy functional as an excitation of the electronic configuration from the ground-state configuration. The excess energy in the electronic system due to this excitation provides the kinetic energy needed to evolve the electronic configuration from φ_0 to χ_0 .

The ionic degrees of freedom in the molecular dynamics Lagrangian will behave like classical degrees of freedom and the ionic configuration will evolve at a constant total energy provided that the forces on the ions are always calculated with the electronic system in the ground state of the instantaneous ionic configuration. The electronic degrees of freedom do not behave like classical degrees of freedom. The constraint of normalisation damps the motion of the electronic degrees of freedom so that energy is continuously removed from the electronic degrees of freedom, forcing the electronic configuration to relax towards its ground state. When the ions are moving energy has to be continuously supplied to the electronic degrees of freedom to overcome the damping and allow the electronic configuration to evolve between the instantaneous ground states. The analysis presented above shows how this energy is provided without removing energy from the ionic degrees of freedom.

The different behaviours of the degrees of freedom associated with the electronic and ionic systems is essential for the success of the molecular dynamics method. If the ionic and electronic degrees of freedom both behaved as classical degrees of freedom then by equipartition all the available energy in the system would be shared equally amongst all the degrees of freedom. In a molecular dynamics total energy pseudo-potential calculation with a plane wave basis set there are typically a factor of 10^4 more electronic degrees of freedom than ionic degrees of freedom. If equipartition occurred the electronic system would have 10^4 times as much thermal energy as the ionic system so that the electronic configuration could only be close to its ground state if the temperature of the ionic system was very close to zero. Energy would fluctuate between the electronic and ionic systems and because of the large number of degrees of freedom associated with the electronic system the electronic system would act as a heat bath for the ionic system. Hence the energy of each ion would vary with time according to a Boltzmann distribution and the constant energy evolution of the ionic system would be destroyed by thermal fluctuations. Only by maintaining a delicate balance between supplying energy to the electronic degrees of freedom and then damping these degrees

of freedom to remove this energy can the electronic configuration move between the instantaneous ground states without continually increasing the energy in the electronic degrees of freedom to the point where fluctuations of energy between the electronic and ionic systems would destroy the accuracy of the ionic trajectories.

4. Error cancellation in the Hellmann–Feynman forces

In the previous section it was shown how the electronic system acquires energy to move between ground states of the instantaneous ionic configuration without removing energy from the ionic system. However, the constant energy evolution of the ionic system still requires that the Hellmann–Feynman forces are calculated only when the electrons are in the instantaneous ground-state configuration and it would appear that the forces on the ions must be correct to an extremely high accuracy at each timestep in order to perform simulations for several thousand timesteps with a negligible loss of energy from the ionic system. It will now be shown that the accuracy of the Hellmann–Feynman forces does not have to be this high because a cancellation of the errors in the Hellmann–Feynman forces takes place when the molecular dynamics equations of motion are used to evolve the electronic degrees of freedom. The contribution to the Hellmann–Feynman force exerted on any ion due to Coulomb interactions between the ions can be calculated to arbitrary accuracy. As there is no error associated with the ionic contributions to the Hellmann–Feynman forces only the contributions to the Hellmann–Feynman forces from the electrons will be considered in this section.

The origin of the cancellation of errors in the Hellmann–Feynman forces will first be described qualitatively and then a quantitative account of the effect will be given. A system containing a single atom which has one occupied electronic orbital will be considered for the qualitative analysis. The molecular dynamics equation of motion for the evolution of the electronic wavefunction is

$$\ddot{\psi} = -(H - \lambda)\psi. \quad (32)$$

If the atom is at rest and the electronic wavefunction is the ground-state wavefunction then $(H - \lambda)\psi = 0$ and the electronic wavefunction will be stationary, as expected. If the orbital is displaced away from the ion the magnitude of the acceleration of the wavefunction would be expected to increase roughly linearly with the displacement of the orbital from the ion for small displacements. If the ion starts to move the orbital will initially lag behind the ion but the acceleration of the orbital will cause the velocity of the orbital to increase until the orbital overtakes the ion. As the orbital overtakes the ion the acceleration of the wavefunction will change sign and the orbital will begin to slow down. Hence if the ion moves at constant velocity the orbital will tend to oscillate around the instantaneous position of the ion. The value of the Hellmann–Feynman force exerted on the ion by the orbital will oscillate around the correct value so that the error in the Hellmann–Feynman force will cancel when averaged over a number of timesteps. The oscillation of the error in the Hellmann–Feynman force will prevent a continuous transfer of energy from the ion to the electronic degrees of freedom.

A first-order equation of motion gives the following expression for the evolution of the electronic orbital

$$\dot{\psi} = -(H - \lambda)\psi. \quad (33)$$

With this equation of motion the velocity of the orbital would be expected to increase

roughly linearly with the displacement of the orbital from the ion. Once the ion has begun to move the orbital will fall further behind the ion until its velocity is equal to the velocity of the ion and then the orbital will remain a fixed distance behind the instantaneous position of the ion. The Hellmann–Feynman force exerted by the orbital on the ion will have a systematic error because the orbital will always lag behind the ion. The ion will appear to be moving in a viscous medium because the damping force exerted by the orbital on the ion is proportional to the velocity of the ion. These qualitative models suggest that the dynamics of the ionic system will be more accurately described when a second-order equation of motion is used to evolve the electronic degrees of freedom than a first-order equation of motion.

The cancellation of the errors in the Hellmann–Feynman forces will now be analysed quantitatively using the system described in § 3. The ions will be assumed to move at constant velocities between positions \mathbf{R}_I^1 and \mathbf{R}_I^2 in a time T . Assuming a linear change in the self-consistent potential with respect to the positions of the ions the Hamiltonian at time t is

$$H(t) = H(\{\mathbf{R}_I^2\}) - [1 - (t/T)]\Delta V_{\text{sc}} \quad (34)$$

where $H(\{\mathbf{R}_I^2\})$ is the Hamiltonian for the ions in positions \mathbf{R}_I^2 , and ΔV_{sc} is the change in the self-consistent potential on moving the ions from positions \mathbf{R}_I^1 to \mathbf{R}_I^2 . The actual Hamiltonian at time t will differ from this expression if the electronic wavefunction at time t is not the instantaneous ground-state wavefunction because the potential generated by the electronic states will not be the self-consistent electronic potential. If the electronic configuration moves too far from the instantaneous ground-state configuration the evolution of the electronic configuration becomes unstable. In the following section a criterion will be developed for the maximum error that can be tolerated in the electronic wavefunction and it will be shown that this restricts the velocity of propagation of the ions.

The ground-state wavefunction at time t , $\psi_0(t)$, to first order in perturbation theory is

$$\psi_0(t) = \chi_0 - [1 - (t/T)] \sum_{n \neq 0} \frac{\langle \chi_n | \Delta V_{\text{sc}} | \chi_0 \rangle}{\epsilon_0 - \epsilon_n} \chi_n \quad (35)$$

where $\{\chi\}$ are the eigenstates of Hamiltonian $H(\{\mathbf{R}_I^2\})$ defined by (12).

The electronic configuration is in the ground state of Hamiltonian $H(t)$ at $t = 0$. It will be assumed that the electronic configuration is stationary at this time but this assumption does not affect the following analysis because the error cancellation in the Hellmann–Feynman forces is independent of the initial velocities of the electronic degrees of freedom. During the time $0 \leq t \leq T$ the electronic configuration evolves according to the molecular dynamics equations of motion

$$\ddot{\psi}(t) = - (H(t) - \epsilon(t))\psi(t) \quad (36)$$

where $\epsilon(t) = \langle \psi(t) | H(t) | \psi(t) \rangle$.

The contribution to the calculated Hellmann–Feynman force exerted on ion I at time t due to the electrons is given by

$$f'_I(t) = \langle \psi(t) | \nabla_I v_I(\mathbf{r} - \mathbf{R}_I(t)) | \psi(t) \rangle \quad (37)$$

whereas the correct contribution to the Hellmann–Feynman force is

$$f_I(t) = \langle \psi_0(t) | \nabla_I v_I(\mathbf{r} - \mathbf{R}_I(t)) | \psi_0(t) \rangle. \quad (38)$$

The operator $\nabla_I v_I(\mathbf{r} - \mathbf{R}_I)$ is not diagonal so the error in the Hellmann–Feynman force is first order with respect to the error in the wavefunctions, as mentioned previously.

Expanding the wavefunction $\psi(t)$ in terms of the basis set $\{\chi\}$

$$\psi(t) = \sum_n c_n(t) \chi_n \quad (39)$$

and substituting this expression into the molecular dynamics equation of motion gives the following equations of motion for the coefficients c_n

$$\ddot{c}_n(t) = -(\varepsilon_n - \varepsilon(t))c_n(t) + \sum_m [1 - (t/T)] \langle \chi_n | \Delta V_{sc} | \chi_m \rangle c_m(t). \quad (40)$$

To first order in the self-consistent potential the coefficient c_0 remains equal to 1 during the interval $0 \leq t \leq T$, all the other coefficients remain of order ΔV_{sc} and $\varepsilon(t)$ is equal to

$$\varepsilon(t) = \varepsilon_0 - [1 - (t/T)] \langle \chi_0 | \Delta V_{sc} | \chi_0 \rangle. \quad (41)$$

If $\langle \chi_0 | \Delta V_{sc} | \chi_0 \rangle$ is much smaller than any of the differences between the eigenvalue ε_0 and the eigenvalues ε_n the equations of motion for the coefficients are approximately given by

$$\ddot{c}_n(t) = -(\varepsilon_n - \varepsilon(t))c_n(t) + [1 - (t/T)] \langle \chi_n | \Delta V_{sc} | \chi_0 \rangle \quad n \neq 0. \quad (42)$$

These equations can be integrated to give the wavefunction at time t as

$$\begin{aligned} \psi(t) = & \chi_0 - \sum_{n \neq 0} \left([1 - (t/T)] \frac{\langle \chi_n | \Delta V_{sc} | \chi_0 \rangle}{\varepsilon_0 - \varepsilon_n} \right) \chi_n \\ & + \sum_{n \neq 0} \left(\frac{\langle \chi_n | \Delta V_{sc} | \chi_0 \rangle}{(\varepsilon_n - \varepsilon_0)^{3/2} T} \sin[(\varepsilon_n - \varepsilon_0)^{1/2} t] \right) \chi_n. \end{aligned} \quad (43)$$

The first two terms in (43) are equal to the instantaneous ground state wavefunction $\psi_0(t)$ so the final term in (43) represents the error in the wavefunction at time t . It can be seen that the error in the wavefunction is oscillatory in time. Hence the errors in the Hellmann–Feynman force exerted on a single ion will be oscillatory in time and the errors will tend to cancel when averaged along the trajectory of the ion so that there will not be a continuous transfer of energy from the ions to the electronic degrees of freedom.

With the approximations introduced above the first-order equations of motion for the evolution of the coefficients c_n are

$$\dot{c}_n(t) = -(\varepsilon_n - \varepsilon_0)c_n(t) + [1 - (t/T)] \langle \chi_n | \Delta V_{sc} | \chi_0 \rangle \quad n \neq 0. \quad (44)$$

Solving for the wavefunction at time t gives

$$\begin{aligned} \psi(t) = & \chi_0 - \sum_{n \neq 0} \left([1 - (t/T)] \frac{\langle \chi_n | \Delta V_{sc} | \chi_0 \rangle}{\varepsilon_0 - \varepsilon_n} \right) \chi_n \\ & + \sum_{n \neq 0} \left(\frac{\langle \chi_n | \Delta V_{sc} | \chi_0 \rangle}{(\varepsilon_n - \varepsilon_0)^2 T} \{1 - \exp[-(\varepsilon_n - \varepsilon_0)t]\} \right) \chi_n. \end{aligned} \quad (45)$$

It can be seen that the error in this wavefunction is single signed and that the error in the wavefunction tends to a constant at large times. The error in the Hellmann–Feynman force exerted on a single ion will always be in the same direction and the error in the force will not average to zero when integrated along the path of the ion so that there will be a continuous transfer of energy from the ions to the electronic degrees of

freedom when a first order equation of motion is used to evolve the electronic degrees of freedom.

The loss of energy from the ionic system becomes second order with respect to the error in the electronic wavefunction when the molecular dynamics equations of motion are used to evolve the electronic degrees of freedom but it is first order with respect to error in the wavefunction when a first-order equation of motion is used to evolve the electronic degrees of freedom. To obtain the most accurate ionic trajectories in a dynamical simulation the electronic degrees of freedom should, therefore, be evolved using the molecular dynamics equations of motion.

The magnitude of the error in the electronic wavefunction is proportional to $\Delta V_{\text{sc}}/T$ when either the first- or second-order equations of motion are used to evolve the electronic degrees of freedom so the error in the wavefunction is proportional to the velocity of the ions. Hence, the magnitude of the error in the electronic wavefunction can be decreased by increasing the masses of the ions with respect to the fictitious mass of the electronic degrees of freedom so that the ions move more slowly with respect to the electronic degrees of freedom.

5. Stability of electronic configuration

The analysis presented in the previous section assumed that the electronic configuration remained close to the instantaneous ground state so that potential remained close to the self-consistent potential V_{sc} . If the error in the coefficient c_n is δc_n and the total change in the coefficient c_n during the movement of the ions from positions \mathbf{R}_i^1 to \mathbf{R}_i^2 is Δc_n then $(\delta c_n/\Delta c_n)\Delta V_{\text{el}}$ is the error in the electronic potential due to the error in the wavefunction. The error in the electronic potential must be smaller than the self-consistent potential V_{sc} or the evolution of the electronic configuration will become unstable because the evolution of the electronic configuration will be driven solely by the electronic potential. The change in the electronic potential at wavevector \mathbf{G} during the movement of the ions from positions \mathbf{R}_i^1 to \mathbf{R}_i^2 , $\Delta V_{\text{el}}(\mathbf{G})$, is roughly $G\Delta R$ times the total electronic potential at wavevector \mathbf{G} , where ΔR is the average distance moved by the ions. Therefore the criterion for stability during the evolution of the electronic configuration for the second-order equation of motion is

$$G\Delta R/(\varepsilon_n - \varepsilon_0)^{1/2}T \ll |V_{\text{sc}}(\mathbf{G})/V_{\text{el}}(\mathbf{G})| \quad (46)$$

and for the first-order equation of motion the criterion for stability is

$$G\Delta R/(\varepsilon_n - \varepsilon_0)T \ll |V_{\text{sc}}(\mathbf{G})/V_{\text{el}}(\mathbf{G})| \quad (47)$$

where $V_{\text{sc}}(\mathbf{G})$ is the self-consistent potential at wavevector \mathbf{G} and $V_{\text{el}}(\mathbf{G})$ is the electronic potential at wavevector \mathbf{G} . The difference in the power law dependence of these equations on $\varepsilon_n - \varepsilon_0$ is due to the different definition of time in the first- and second-order equations of motion.

The value of $|V_{\text{sc}}(\mathbf{G})/V_{\text{el}}(\mathbf{G})|$ can be calculated from the dielectric function. If the magnitude of the dielectric function is large $|V_{\text{sc}}(\mathbf{G})/V_{\text{el}}(\mathbf{G})|$ is inversely proportional to the dielectric function. At small wavevectors the magnitude of the dielectric function varies as $1/G^2$ so that $|V_{\text{sc}}(\mathbf{G})/V_{\text{el}}(\mathbf{G})|$ is proportional to G^2 . According to (46) and (47) the largest velocity of the ions at which the electronic configuration evolves stably is proportional to the magnitude of the smallest reciprocal-lattice vector. The magnitude of the smallest reciprocal-lattice vector is inversely proportional to the magnitude of

largest unit cell vector hence the largest permissible velocity of propagation for the ions is inversely proportional to the longest length of an edge of the unit cell. The smallest value of $\varepsilon_n - \varepsilon_0$ can also depend on the size of the system. If the system has a gap in the energy spectrum then the minimum value of $\varepsilon_n - \varepsilon_0$ is independent of the size of the system but if there is no gap in the spectrum the minimum value of $\varepsilon_n - \varepsilon_0$ will get smaller as the size of the system increases. However the difference between two wavefunctions on the same branch of the band structure is roughly proportional to the difference between their energies which suggests that the error in the electronic wavefunction due to replacing the groundstate wavefunction by an excited state wavefunction of energy ε_n is roughly proportional to $\varepsilon_n - \varepsilon_0$ provided that $\varepsilon_n - \varepsilon_0$ is small. In this case the stability criterion should not be particularly sensitive to the minimum value of $\varepsilon_n - \varepsilon_0$ provided that the excited-state many-particle product wavefunction χ_n differs from the ground-state wavefunction χ_0 by electron-hole pair excitations in which the electron and hole occupy the same band.

The magnitude of the errors in the Hellmann-Feynman forces when the second-order equation of motion is used to evolve the electronic configuration will be reduced further by normalisation of the wavefunctions. Any form of damping will reduce the amplitude of the oscillatory part of the electronic wavefunction faster than the slowly varying part. The velocities associated with the errors in the wavefunction are larger than the velocity of the ground-state wavefunction so that damping due to the constraint of normalisation will tend to reduce the relative magnitude of the error in the wavefunction.

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