PHYSICAL REVIEW B VOLUME 53, NUMBER 16 15 APRIL 1996-II

Alternative equations of motion for dynamical simulated annealing of the density functional

J. C. Greer
Department of Chemistry, Trinity College, Dublin 2, Ireland

(Received 15 November 1995)

An alternative scheme for *ab initio* molecular-dynamics simulations using the density-functional expression for the total electronic energy is proposed. A constrained procedure emerges where only the total electronic density need be dynamically propagated. When energy dissipation is removed from the minimization dynamics, the method becomes equivalent to the microcanonical sampling of the functional integral representation of interacting fermions and bosons.

I. INTRODUCTION

The Car-Parrinello *ab initio* molecular-dynamics (*ai*MD) approach has provided an alternative means for solution of the electronic structure problem and simultaneously allows for energy minimization with respect to the nuclear positions.[1] The method relies on ideas based upon the concept of simulated annealing developed for minimization problems,[2] however, the Monte Carlo generation of system configurations is replaced by a dissipative dynamics scheme. Hence the *ai*MD procedure is also referred to as dynamical simulated annealing. Within the context of density-functional theory, the Born-Oppenheimer energy for a system may be represented as

$$E[\psi_i,R_I]=\sum_i \int \psi_i^*(\mathbf{r})\left[-\frac{\hbar^2}{2m_e}\nabla^2\right]\psi_i(\mathbf{r})d\mathbf{r} + U[\rho(\mathbf{r}),\{R_I\}], \tag{1}$$

where the ψ_i are occupied single-particle orbitals, ρ is the total electron density, $\mathbf{r}$ are electron positions, and $\{R_I\}$ is the set of nuclear coordinates. The Car-Parrinello strategy is to introduce a minimization dynamics for the electronic and nuclear degrees of freedom (for self-consistent electronic solutions, the nuclear dynamics becomes classical dynamics on the Born-Oppenheimer surface). The electronic wave functions evolve according to the following expression:

$$\mu\ddot{\psi}_i(\mathbf{r},t)=-\delta E[\psi^*,\psi]/\delta\psi_i^*(\mathbf{r},t)+\sum_j \epsilon_{ij}\psi_j(\mathbf{r},t), \tag{2}$$

where E is the total electronic energy of the system and the ϵ_{ij} are Lagrangian multipliers introduced to enforce orthogonality of the single-electron wave functions. Although Car and Parrinello developed the method using the density functional, it is clear from the above expression that any means of describing the electronic energy may be used within their approach.

In the following, an analogy between *ab initio* molecular-dynamics simulations using Hartree-Fock theory[3] and microcanonical simulations applied to interacting fermions and bosons[4] is reviewed. This analogy is achieved by defining an alternative fictive dynamics scheme whereby the potential functions of the Hartree-Fock operator become the degrees of freedom for the fictive dynamics. The method is not immediatelly extendable to the density-functional expression due to the choice of canonical variables within the scheme. The purpose of this paper is to identify a related scheme for the density-functional expression by choosing the total electronic density as a ''position coordinate.'' The result is a simple procedure requiring only the dynamical propagation of a single degree of freedom: the total electronic density. Application of the method is demonstrated for atomic systems.

II. MICROCANONICAL SIMULATIONS OF FERMIONS AND HARTREE-FOCK CALCULATIONS

Consider the case of a quantum field theory with an action of the form

$$S=\sum \overline{\psi}h[\phi]\psi+S_B[\phi], \tag{3}$$

where $h[\phi]$ describes the fermions plus interaction and S_B is the free bosonic action. It is desired to generate a large number of fermion ψ and boson ϕ field configurations for the stochastic evaluation of the partition function. The microcanonical approach to the problem[4] introduces a dynamics through the fictive Lagrangian

$$L=\tfrac{1}{2}VM[q]V-\omega^2Q^2+\tfrac{1}{2}\mu v^2-U[q] \tag{4}$$

with conjugate variables $\{MV,Q\}$ and $\{\mu v,q\}$. The Lagrangian is associated with the field theoretic problem through the following identifications:

$$V\leftrightarrow\psi, \quad q\leftrightarrow\phi,$$

$$\tfrac{1}{2}M[q]\leftrightarrow h[\phi], \quad U[q]\leftrightarrow S_B[\phi].$$

The Euler-Lagrange equations of motion are

0163-1829/96/53(16)/10651(5)/$10.00

$$\ddot{\phi} = -\frac{\delta}{\delta\phi}(S_B[\phi] - \psi^* h[\phi]\psi), \tag{5}$$

$$\frac{d}{dt}(h[\phi]\psi) = -\omega^2\psi.$$

For microcanonical simulations, it is desired to generate field configurations via the fictive dynamics scheme. Instead of the introduction of a dissipative term as in an *ai*MD approach, a harmonic potential $\omega^2 Q^2$ is introduced for the fermionic degrees of freedom to aid in the generation of field configurations. It can be shown that expectation values of functionals of the boson fields ϕ are not changed by the introduction of these additional terms.

The steps leading to a Lagrangian function of the form of Eq. (4) will now be shown as given for Hartree-Fock *ai*MD in Ref. 3. The energy expectation value for the Hamiltonian operator of the quantum Coulomb problem in a single Slater determinant is rewritten as an energy density

$$E = \int d\mathbf{r}\mathcal{E}(\mathbf{r}),$$

$$\mathcal{E}(\mathbf{r}) = \sum_{ij} \left\{ \psi_i^*(\mathbf{r}) \left[\gamma_{ij} h_1(\mathbf{r}) + 2\sum_{kl} \Gamma_{ijkl}\phi_{kl}(\mathbf{r}) \right] \psi_j(\mathbf{r}) - \sum_{kl} \Gamma_{ijkl}\psi_i^*(\mathbf{r})\phi_{kl}(\mathbf{r})\psi_j(\mathbf{r}) \right\}, \tag{6}$$

where h_1 is the kinetic energy and one-body potentials, $\gamma_{ij} = \delta_{ij}$ is the one-particle density matrix, $\Gamma_{ijkl} = 1/2[\gamma_{ij}\gamma_{kl} - \gamma_{il}\gamma_{kj}]$ is the two-particle density matrix, and

$$\phi_{ij}(\mathbf{r}) = \int d\mathbf{r}' \frac{\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{7}$$

are Coulomb and exchange potentials. The first term in Eq. (6) is the sum of the single-particle energies and the second term corrects the overcounting of the two-body potentials. The energy density is rewritten after two steps. Firstly, the Hartree-Fock operator is written as

$$h_{ij}[\phi] = \gamma_{ij} h_1(\mathbf{r}) + 2\sum_{kl} \Gamma_{ijkl}\phi_{kl}(\mathbf{r}). \tag{8}$$

Secondly, the correction for the overcounting of the two-body terms is rewritten by using

$$\psi_i^*(\mathbf{r})\psi_j(\mathbf{r}) = \hat{V}^{-1}\phi_{ij}(\mathbf{r}). \tag{9}$$

For the Coulomb potential, the inverse operator is simply defined with

$$\hat{V}^{-1}V(\mathbf{r},\mathbf{r}') = -\frac{1}{4\pi}\nabla^2 \frac{1}{|\mathbf{r}-\mathbf{r}'|} = \delta^3(\mathbf{r}-\mathbf{r}'). \tag{10}$$

The energy density can now be expressed as

$$\mathcal{E}(\mathbf{r}) = \sum_{ij} \psi_i^*(\mathbf{r}) h_{ij}[\phi]\psi_j(\mathbf{r}) + \frac{1}{4\pi}\sum_{ijkl} \Gamma_{ijkl}\phi_{ij}(\mathbf{r})\nabla^2\phi_{kl}(\mathbf{r}). \tag{11}$$

In this form, the Hartree-Fock equations resemble a field theory of fermions interacting with a three-dimensional, massless boson field. Through the identifications

$$V \leftrightarrow \psi, \quad q \leftrightarrow \phi, \quad \tfrac{1}{2}M[q] \leftrightarrow h[\phi],$$

contact is made with the microcanonical approach. The corresponding equations of motion are modified in two ways: a harmonic potential is not introduced but orthogonality constraints for the wave functions are introduced. The Lagrangian multipliers to enforce orthogonality are included in the usual way leading to the modified equations of motion:

$$\ddot{\phi} = -\frac{\delta}{\delta\phi}(S_B[\phi] - \psi^* h[\phi]\psi),$$

$$\frac{d}{dt}\{(h[\phi] - \epsilon)\psi\} = 0. \tag{12}$$

The Euler-Lagrange equation for ψ is rewritten as

$$(\dot{h}[\phi] - \dot{\epsilon})\psi = (\epsilon - h[\phi])\dot{\psi}. \tag{13}$$

Using the first-order approximation to the time derivative, the equation becomes

$$(\Delta h[\phi] - \Delta\epsilon)\psi = (\epsilon - h[\phi])\Delta\psi. \tag{14}$$

It is seen that the first-order approximation leads to the first-order perturbative correction to the eigenvalues and wave functions. Within this approach, the potential functions ϕ_{ij} are propagated dynamically while the wave functions are corrected by treating the change in the potentials as a perturbation; further details can be found in Ref. 3.

III. AN ALTERNATIVE DYNAMICS SCHEME FOR THE DENSITY FUNCTIONAL

For the Car-Parrinello scheme, a ficticious Lagrangian is defined as

$$L = \sum_i \frac{1}{2}\mu \int |\dot{\psi}_i|^2 d\mathbf{r} + \frac{1}{2}\sum_I M_I \dot{R}_I^2 - E[\psi_i, R_I], \tag{15}$$

with conjugate variables $\{p,q\} = \{\mu\dot{\psi}, \psi\}$ and $\{P,Q\} = \{M\dot{R}, R\}$ and μ is a ficticious mass variable. The electronic and nuclear equations of motion then follow:

$$\mu\ddot{\psi}_i(\mathbf{r},t) = -\delta E/\delta\psi_i^*(\mathbf{r},t) + \sum_j \epsilon_{ij}\psi_j(\mathbf{r},t), \tag{16}$$

$$M_I \ddot{R}_I = -\nabla_I E, \tag{17}$$

where the Lagrangian multipliers ϵ_{ij} have been introduced to enforce the orthonormality of the single-particle wave functions. The expression for the total density in terms of the single-particle wave functions is

$$\rho(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r})|^2, \tag{18}$$

allowing variations of the single-particle functions to be represented as variations of the total density. The Euler-Lagrange equation of motion for the single-particle functions may be explicitly written as

$$\mu\ddot{\psi}_i(\mathbf{r},t) = -\delta E/\delta\rho(\mathbf{r},t) + \sum_j \epsilon_{ij}\psi_j(\mathbf{r},t), \tag{19}$$

$$\left[\mu\frac{\partial^2}{\partial t^2} - \frac{\hbar^2}{2m_e}\nabla^2 + \phi_H(\mathbf{r},t) + \phi_{\mathrm{xc}}(\mathbf{r},t)\right]\psi_i(\mathbf{r},t) = \epsilon_i(t)\psi_i(\mathbf{r},t), \tag{20}$$

with ϕ_H the Hartree potential including any external potentials and ϕ_{xc} the exchange-correlation potential within the local density approximation. Note that when

$$\mu\frac{\partial^2}{\partial t^2}\psi_i(\mathbf{r},t) = 0, \tag{21}$$

the equations of motion reduce to the Kohn-Sham self-consistent equations for the single-particle wave functions.[5] Car and Parrinello use the Verlet algorithm[6] for the time integration and introduce the method of Ryckaert, Ciccotti, and Berendsen[7] to enforce the constraints.[8] In some implementations of the algorithm, only a ''partially constrained'' dynamics is employed,[9,10] allowing the single-particle functions to be propagated without the constraint of orthonormality. After a single step of the time evolution, orthogonality is restored explicitly by means such as the Gram-Schmidt procedure. Alternative to the dynamics procedure for the electronic degrees of freedoms, a reformulation of the wave-function optimization in terms of constrained minimization procedures has been given[11] for situations where it is clear that there are not many local minima: for these cases, simulated annealing strategies are not appropriate for optimization of the single-particle wave functions.

It can be observed that in partially constrained schemes the orthogonality constraints are not present during a dynamics update. Consider the diagram in Fig. 1(a), which is intended as a schematic representation of phase space for a Car-Parrinello fictive dynamics scheme. The energy is a constant of motion dependent on the ''momenta'' $p = \mu\dot{\psi}$ and ''positions'' $q = \psi$. The closed path is intended to represent a constant energy trajectory through phase space along which the orthonormality constraint is respected. As the simulation progresses, kinetic energy is removed from the system and, based upon the ideas of simulated annealing, the final zero temperature self-consistent equations will be a solution to the Kohn-Sham equations, the correct ground-state energy. Note, however, if the constraint of orthonormality is relaxed, the dynamics updates are not restricted to the constrained energy surface that is depicted in Fig. 1(a). The nondynamical step of orthogonalization returns to an energy surface in phase space where the constraints are satisified, but for new values of $\{q,p\}$. The nonconstrained dynamics update and the following nondynamical orthogonalization of the wave functions can result in an erratic search of the functional space.

It will now be shown how a dynamical simulated annealing approach can be maintained for the electronic structure problem but where it is only necessary to dynamically propagate one degree of freedom. This can be achieved following the approach previously described for Hartree-Fock simulations. A single-particle Hamiltonian operator is defined as

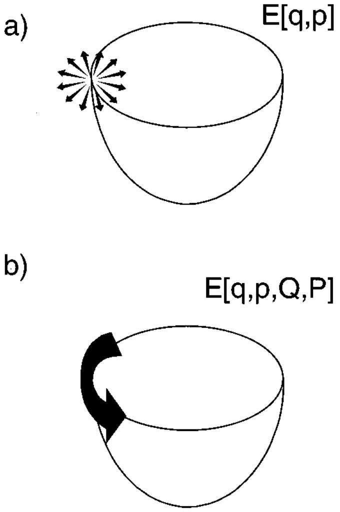

FIG. 1. Schematic representations of phase space for *ab initio* molecular dynamics simulations. (a) Using the equation of motion given in Eq. (3), the system propagates along a constant energy surface. If the orthogonality restaints are lifted, the dynamics updates will leave the constrained energy surface. (b) For the proposed method, the dynamics defines a fictive dynamics for the total electron density and the one-electron functions are perturbatively corrected. The energy remains on the constrained energy surface to within first order in the perturbation.

$$h[\phi] = -\frac{\hbar^2}{2m_e}\nabla^2 + \phi(\mathbf{r}), \tag{22}$$

$$\phi(\mathbf{r}) \equiv \phi_H(\mathbf{r}) + \phi_{\mathrm{xc}}(\mathbf{r}).$$

The density-functional energy for the system is written in terms of the single-particle Hamiltonian operator as

$$E = \sum_i^{\mathrm{occ}} \int d\mathbf{r}\,\psi_i^* h[\rho]\psi_i - U[\rho], \tag{23}$$

with

$$U[\rho] = \frac{1}{2}\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' - \int \rho(\mathbf{r})\{\epsilon_{\mathrm{xc}}[\rho] - \mu_{\mathrm{xc}}[\rho]\}d\mathbf{r} \tag{24}$$

and ϵ_{xc} is the exchange-correlation energy per electron for a uniform electron gas and $\mu_{\mathrm{xc}} = \delta(\rho\epsilon_{\mathrm{xc}}[\rho])/\delta\rho$. When the ψ_i satisify the Kohn-Sham equations, Eq. (23) is the density-functional energy within the local density approximation. A fictive Lagrangian for the electronic degrees of freedom can now be written as

$$L = \tfrac{1}{2}VM[q]V + \tfrac{1}{2}\mu v^2 - U[q] \tag{25}$$

with the identifications

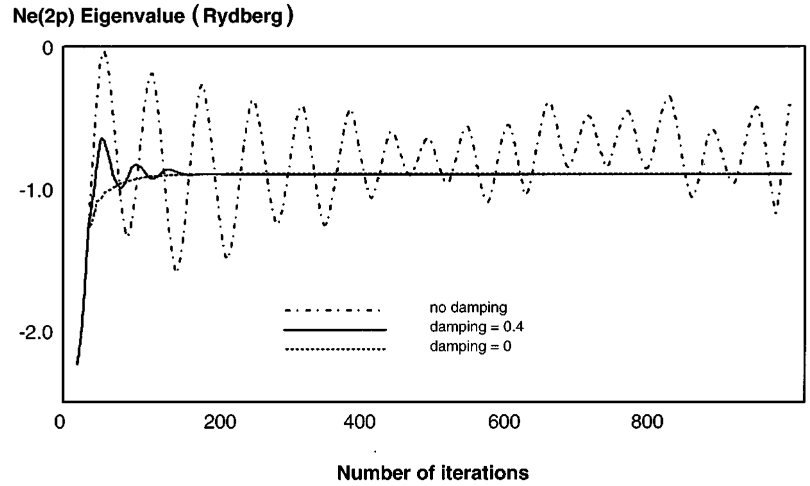

FIG. 2. Calculation of the Ne$(2p)$ eigenvalue. The dynamics are performed with three values of damping: (i) no damping, $\gamma=1$, (ii) intermediate damping, $\gamma=0.4$, (iii) overdamped, $\gamma=0.0$.

$$V\leftrightarrow\psi,\quad q\leftrightarrow\rho,$$

$$v\leftrightarrow\dot{\rho},\quad \tfrac{1}{2}M[q]\leftrightarrow h[\rho].$$

The momenta and positions $\{\mu v,q\}$ are conjugate variables whereas the momenta $M[q]V$ are for free particles with a mass term dependent on the positions q. Variation of the action with introduction of the orthonormality constraints,

$$\delta I=0\rightarrow\delta\int dt\left\{\sum^{\text{occ}}\int d\mathbf{r}\psi^*(h[\rho]-\epsilon)\psi+\frac{1}{2}\mu\dot{\rho}^2-U[\rho]\right\}$$
$$=0, \tag{26}$$

leads to the Euler-Lagrange equations of the same form as Eq. (12):

$$\mu\ddot{\rho}=-\frac{\delta}{\delta\rho}\left\{U[\rho]-\sum^{\text{occ}}\int d\mathbf{r}\psi^*h[\rho]\psi\right\}, \tag{27}$$

$$(h[\rho]-\epsilon)\dot{\psi}=(\dot{\epsilon}-\dot{h}[\rho])\psi. \tag{28}$$

Equation (27) allows the updating of the density based upon variations of the total constrained energy. For dynamical simulated annealing strategy, the velocities $\dot{\rho}$ will be quenched, allowing the system to come to rest in energy minima. When a minimum is encountered, the accelerations $\ddot{\rho}$ become zero and the equation of motion becomes the ground state of the density-functional expression. However, the perturbative update Eq. (28) allows a new approach to the wave function updates. The equation of motion is again rewritten to first order as

$$(h[\rho]-\epsilon)\Delta\psi=(\Delta\epsilon-\Delta h[\rho])\psi. \tag{29}$$

If Eq. (18) relating the density to the single-particle functions is satisified as an initial condition, this property will be preserved within the accuracy of the perturbation correction to the wave functions throughout the time evolution of the system. Corrections to this condition can be applied based upon usual considerations with respect to the errors introduced by a finite time step. Similar to the Hartree-Fock dynamics approach described previously, the constrained dynamics may be summarized as follows: Eq. (27) defines a dynamics allowing the density to be propagated for a single time step. The corresponding change in the density gives rise to a change in the potential energy terms. The change in the potential energy due to the fictive dynamics for the density is then used to determine a perturbative correction to the single-particle functions and energies. In this respect, the single-particle functions are ''dragged along'' by the density dynamics. In this way, the trajectory is restricted to first order to the constrained energy surface shown schematically in Fig. 1(b).

IV. A NUMERICAL EXAMPLE

To illustrate the method, a simple density-functional theory calculation for the neon atom was performed. The exchange-correlation potential was chosen to be the corresponding exchange potential for a homogeneous electron gas (this does not change the form of the equations to be solved). Spherical symmetry was assumed and the calculation was performed with numerical wave functions defined on a pseudologarithmic grid. Dynamical simulated annealing was performed with velocity scaling of the form

$$v_\gamma(t)=\gamma v(t) \tag{30}$$

after every ten iterations with t the simulation time and γ a parameter chosen to control the rate of energy loss. The time step was taken to be $\delta t=0.05$ in units where the fictitious mass $\mu=1$. Initial conditions were chosen as follows: starting wave functions and their corresponding eigenvalues for the singly charged neon cation were taken as an initial guess and a zero initial velocity was assigned to $\dot{\rho}$. Convergence to the correct single-particle eigenvalues to four significant figures was reached and the final integrated density was also correct for the number of particles to better than four figures. In Fig. 2, the $2p$ eigenvalue as a function of simulation time is shown for three different damping factors. To avoid accumulation of error due to the first-order perturbative updates, corrected eigenfunctions and eigenvalues were generated by solving the Schrödinger equation with the current potential arising from the current density ρ after typically

25–50 iterations (the exact value dependent on simulation time *t* and the damping). The resulting number of solutions to the Schrödinger equation is comparable to that required in standard self-consistent field methods. However, the number of times to correct the eigenfunctions and vectors can be reduced by judicious choice of time step and initial conditions. Alternatively, orthogonalization of the wave functions and corrected eigenvalues may be achieved by other means. In any event, for the simulations presented here, the correction to the wave functions and eigenvalues due to the small changes in the density at longer times was negligible for the cases where damping was present. In *ai*MD simulations, the perturbation arising from the propagation of the nuclear coordinates is also anticipated to be small, hence corrections to wave functions and eigenvalues are not anticipated to be necessary except for long run times and then only after a large number of nuclear coordinate updates. In Fig. 2, the desired fictive dynamics for the electronic density is displayed. For overdamping $\gamma = 0.0$, the eigenvalue smoothly converges to the correct value. If the damping is chosen to be $\gamma = 0.4$, the calculated eigenvalue is seen to oscillate about the correct value as the simulation progresses and converges to the correct solution as the ‘‘velocity’’ is damped. This is the behavior necessary for dynamical simulated annealing. The purpose of the fictive dynamics is to search the functional space to locate the true global minimum; the fictive dynamics allows the simulation to escape local minima and eventually to become trapped in the correct ground state based upon statistical mechanical arguments. Without damping $\gamma = 1.0$, the simulation is seen to oscillate at all times without convergence to the correct eigenvalue.

V. CONCLUSION

Expressing the fictive dynamics for different approaches to quantum many-body problems (namely, density-functional theory, the Hartree-Fock approximation, and the microcanonical representation of interacting fermions and bosons) in the above outlined way leads to a common framework for the computation of the properties of quantum systems. The herein described method of imposing the orthogonality constraints on the single-particle wave functions allows for a dynamical simulated annealing scheme for the density functional expression for electronic energies while propagating only one degree of freedom: this allows one to directly minimize the density functional with respect to density as opposed to the Kohn-Sham orbitals. For the case of microcanonical simulations, the method of constraining the fermion updates leads to a straightforward means of sampling over orthogonal fermion states.

ACKNOWLEDGMENT

This work was made possible by an endowmemt to Trinity College Dublin from Hitachi, Ltd.

---

[1] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[2] S. Kirkpatrick, C. D. Gelatt, and M. P. Vecchi, Science **220**, 671 (1983).

[3] J. C. Greer, Theor. Chim. Acta **88**, 363 (1994).

[4] J. Polonyi and H. W. Wyld, Phys. Rev. Lett. **51**, 2257 (1983).

[5] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[6] L. Verlet, Phys. Rev. **159**, 98 (1967).

[7] J. P. Ryckaert, G. Ciccotti, and H. J. C. Berendsen, J. Comput. Phys. **23**, 327 (1977).

[8] I am endebted to Professor Stefano Baroni, CECAM, for clarification on this point.

[9] L. J. Clarke, Theor. Chim. Acta **84**, 325 (1993), and references therein.

[10] M. C. Payne, J. D. Joannopoulos, D. C. Allan, M. P. Teter, and D. H. Vanderbilt, Phys. Rev. Lett. **56**, 2656 (1986).

[11] I. Štich, R. Car, M. Parrinello, and S. Baroni, Phys. Rev. B **39**, 4997 (1989).