First-Principies Molecular Dynamics

José R. Mohallem, Reinaldo O. Vianna, and Hélio Chacham
Departamento de Física, ICEx, Universidade Federal de Minas Gerais
C.P. 702, 30161 Belo Horizonte, MG, Brazil

We describe first principles methods to simulate the dynamics of molecular and condensed matter systems within the Car-Parrinello scheme. Three approaches are presented: the Density Functional Theory (DFT) approach, the Hartree-Fock (HF) approach, and the Valence-Bond (VB) approach. The algorithms for each approach are described, as well as some applications.

I. Introduction

Quantum Molecular Dynamics (QMD) means the study of the dynamics of atoms in molecules and solids from first principles, within the Born-Oppenheimer (BO) approximation. The knowledge of the microscopic forces on each atom can yield accurate descriptions of the electronic structure, optical properties, molecular and crystal geometries, reaction paths, cluster formation, etc.[l,2].

Two approaches have appeared in the literature to perform QMD calculations. One is the "classical" potential surface (PS) approach where the forces on the atoms are obtained from the gradients of the PS of the solid or molecule, and the PS is obtained from fixed-geometry calculations. The other, and more recent, approach is the Car-Parrinello (CP) method[1], where both the electronic and the configurational degrees of freedom are treated in a common footing, allowing a unified molecular dynamics (MD, also called simulated dynamics, SD) formulation. This permits to deal with the entire nuclei-electron problem within a single first-principles calculation. This article is a review of the techniques that use the CP approach to the QMD of molecules and solids.

Devised to be used in condensed matter calculations within the density functional theory (DFT), the CP approach bases its computational efficiency on the use of plane-wave basis sets and fast Fourier transform techniques. Also, the plane-wave basis set permits the use of the Hellmann-Feynman theorem to compute the forces

on the nuclei directly from the electrostatic potential, and the computation of the nuclear motion becomes a straightforward task. However, the description of finite systems as molecules or clusters requires huge plane-wave basis sets. In this case, localized basis sets are more appropriate.

The use of localized basis sets such as Gaussian-type-orbitals (GTO), although more adequate for finite-size systems, poses the additional problem of calculating the corrections (Pulay corrections) to the forces obtained from the Hellmann-Feynman theorem (He-Fe forces). The corrections are necessary because localized basis sets are parametrically dependent on the position of the nuclei, and He-Fe theorem does not apply. An alternative procedure is to devise a localized basis set that is not centered at the nuclei, such as the floating-GTO set. However, the calculation of matrix elements is more difficult in this case, and a new set of parameters have to be optimized (that is, the position of the GTO's).

The CP approach was originally designed for DFT calculations of condensed matter problems such as structural properties of solids, glasses and liquids. The extension of the CP approach to Hartree-Fock calculations of molecular physics problems has been proven to be feasible and worth doing[3-5] (The use of the DFT is not appropriate in cases where excited states are relevant). Hartke and Carter[5a] used the CP-MD to study the formation of Na_4 clusters with spin eigenstate-dependent HF. Our group has developed CP

algorithms for electronic structure and geometry optimization within the HF formalism[3,4]. We also have developed GTO basis sets that nearly satisfy the He-Fe theorem[6]. These basis sets, which have standard sizes, are adequate for CP calculations of finite systems such as molecules and clusters.

In order to extend the CP methodology to QMD problems of real interest, it becomes necessary to resort to correlation methods, since the HF wavefunctions do not describe molecular dissotation properly. Hartke and Carter reported[5b] a generalized VB (GVB) MD study of Na$_4$ clusters. The approach of Ref.[5b], however, is restricted to a single covalent structure. Our group has developed a VB-MD approach to deal with an arbitrary number of ionic and covalent structures. Some results with this new method are presented at the end of this review.

II. Sketch of the CP procedure

Consider a system of m electrons and M nuclei. The BO total energy functional can be written as

$$E = E[\psi_{\vec{r}_i}\{\vec{\alpha}\}; \{\vec{R}\}], \qquad (1)$$

where the electronic wavefunction ψ depends on the electron coordinates $\vec{r}_i$ and on a set of parameters {Z}. The energy functional also depends parametrically on a set of nuclear coordinates $\{R\}$.

Suppose now that we identify the parameters $\{\vec{\alpha}\}$ and $\{\vec{R}\}$ with a set of generalized coordinates of a ficticious classical system,

$$\{q_k\} = \{\vec{\alpha}\} \cup \{\vec{R}\} . \qquad (2)$$

We will also suppose that the potential energy of this ficticious system is the total energy functional E = $E[\{qk\}]$. Including dissipative forces in the ficticious system, and ascribing a mass m_k to each degree of freedom, the dynamics of the system will be defined by the Lagrangean

$$L = e^{\gamma t/2}\left\{\sum_k \frac{1}{2}m_k\dot{q}_k^2 - E[\{q_k\}]\right\}, \qquad (3)$$

where the exponential factor accounts for the dissipative forces. If we impose additional constraints to the dynamics of the q_k (for instance, orthonormality constraints on the wavefunction), the equations of motion

(EM) derived from (3) are

$$m_k\ddot{q}_k - \frac{1}{2}m_k\gamma\dot{q}_k = -\frac{\partial E}{\partial q_k} + g_k, \qquad (4)$$

where g_k is the k-th component of the constraint force.

If the γ_k for the electronic degrees of freedom are not null (that is, the dynamics is dissipative), we have

$$\frac{\partial E}{\partial q_k} = g_k, \quad t \to \infty$$

This is exactly the secular equation corresponding to the minimization of $E[\{q_k\}]$, whatever approximation is used for E (Hartree-Fock, DFT, etc.). Therefore, the integration of the EM permits us obtain the eigenvalues and eigenfunctions of the electronic system.

Concerning the configurational degrees of freedom, Eq.(4) allows us either to obtain the real dynamics the nuclei (if $\gamma = O$) or the equillibrium geometry (if $\gamma \# 0$). In either case we must calculate

$$-\frac{\partial E}{\partial R} = \text{He - Fe force} + \text{Pulay correction.} \qquad (5)$$

The last term in (5) is very costly and should be made negligible by a proper choice of basis functions, as discussed in the previous section.

III. Molecular dynamics in the DFT approach

Density Functional Theory (DFT) is based on a theorem[7] that states that the ground state energy of a many-electron system is a functional of the electron density. It is also shown[8] that it is possible to map the many-electron problem into a system of non-interacting electrons with the same electron density and subjected to the effective potential

$$V_{eff}(\vec{r}) = V(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|}d\vec{r}' + \frac{\delta E_{xc}}{\delta p} , \qquad (6)$$

where $V(\vec{r})$ is an external potential and E$_{xc}$ is the exchange-correlation part of the total energy functional. As E$_{xc}$ is not known, it is usually approximated by the exchange-correlation energy of the homogeneous electron gas,

$$E_{xc}[\rho] = \int \rho(\vec{r})\epsilon_{xc}(\rho)d\vec{r} . \qquad (7)$$

This is the so-called local density approximation (LDA) to the DFT. If we write the electron density in terms of the electron orbitals of the non-interacting system,

$$\rho = \sum_i n_i\psi_i^*\psi_i , \qquad (8)$$

the minimization of the energy functional leads to the Kohn-Sham equations

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}\right)\psi_i = \epsilon_i\psi_i \ .$$

(9)

The original Car-Parrinello procedure[1] combines DFT with MD. The DFT total energy

$$E[\rho, \{\vec{R}_\nu\}] \;=\; 2\sum_i \left\langle \psi_i | -\frac{1}{2}\nabla^2 + V|\psi_i \right\rangle + \frac{1}{2}\int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}\,d\vec{r}' +$$
$$+ \int \rho(\vec{r})\epsilon_{xc}(\rho)d\vec{r} + \frac{1}{2}\sum_{\mu,\nu}\frac{Z_\mu Z_\nu}{|\vec{R}_\mu - \vec{R}_\nu|}$$

(10)

is taken as the ficticious potential energy in **(3)**. The nuclear coordinates and the parameters of the orbitals ψ_i play the role of the generalized coordinates q_k. The Lagrangean (3), together with the orthonormality constraints

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \ ,$$

(11)

lead to the equations of motion

$$\mu_i\ddot{\psi}_i - \frac{1}{2}\mu_i\gamma_i\dot{\psi}_i = -\frac{\delta E}{\delta\psi_i^*} + \sum_k \lambda_{ik}\psi_k$$

(12a)

$$M_I\ddot{\vec{R}} - \frac{1}{2}M_{I\gamma}\dot{\vec{R}} = -\vec{\nabla}_{R_I}E \ .$$

(12b)

While the dynamics associated with (12a) is ficticious, the nuclei dynamics described by (12b) can be the real dynamics of the system if $\gamma = 0$ and MI correspond to the masses of the nuclei. On the other hand, if we keep the dissipative forces in both (12a) and (12b), time evolution $(t \to \infty)$ makes the left side of (12a) and (12b) vanish. Eq. (12a) then becomes the Kohn-Sham equation (8) after diagonalization of the Lagrange multiplier matrix λ_{ij}, and (12b) becomes the condition of optimal geometry, $\vec{\nabla}_{R_I}$ E = 0.

In the actual calculations, the orbitals ψ_i are expanded in a plane-wave basis set. With that, equations (12a) become a set of equations for the expansion coefficients $c_{i,\vec{k}}$. These equations are numerically integrated simultaneously with eqs.(12b), mantaining the orbitals ψ_i as (approximate) solutions of the Kohn-Sham equations and generating trajectories for the nuclear motion.

Self-consistency and nuclear relaxation are simultaneously achieved in the CP approach. Further, as we need to solve (12a) just for the occupied orbitals, the CP approach demands less computational time than the traditional SCF approach.

The CP procedure described above has been applied to a number of problems concerning structural properties and dynamics of clusters, liquids, amorphous semiconductors and surfaces[2].

IV. Molecular dynamics **in the Hartree-Fock approach**

The application of the CP-MD to Hartree-Fock (HF) calculations was made simultaneously by our group[3,4] and by Hartke and Carter[5]. Our main goal was to develop a methodology to apply the CP approach to the problems where the HF method is more appropriate than DFT. Hartke and Carter aimed at qualitatively correct quantum mechanical MD description of molecular systems, in particular Na_4 cluster formation. We initially centered our efforts in building an efficient, stable, and accurate algorithm for simultaneous optimization of the geometry and the wavefunction of molecular systems, successfully tested on diatomics such as LiH, Li_2, BH, FH. In the following, we describe our HF-MD procedure.

In the HF approach, each electron of a N-electron system move as an independent particle in an effective potential generated by the nuclei and the other elec-

trons. This model gives rise to a set of one-electron equations (the HF equations) obeyed by the orbitals. The HF equations result from the minimization of the total energy functional with respect to the variation of a wavefunction that consists of the anti-symmetrized product of one-electron orbitals.

The (BO, non-relativisic) total energy of a molecular system of $N = 2m$ (closed-shell) electrons and Q nuclei is written as

$$E = 2 \sum_a^m h_{aa} + \sum_a^m \sum_b^m (2J_{ab} - K_{ab}) + \sum_{A,B}^Q \frac{Z_A Z_B}{R_{AB}} , \quad (13)$$

where we used standard notation[10].

In the following, we will make explicit the expansion of the HF orbitals in a set of basis functions, and obtain the equations of motion (EM) for the expansion coefficients. Notice that this approach is different from the one used in the previous section, where we obtained the EM for the whole wavefunction (see eq. (12a)). The orbitals are expanded as[4]

$$\psi_a = \sum_A \sum_\sigma \sum_i f_{aA\sigma i} \phi_\sigma(\alpha_i, \vec{r}_A) . \quad (14)$$

Here, $\phi_\sigma(\alpha_i, r')$ is a GTO with exponent cri, σ symmetry $(s, p, d, ...)$, and centered at the nucleus A. The set of exponents $\{\alpha_i\}$ is determined by some prescription[4] and they are not taken as variational parameters. The total energy becomes a functional of the expansion coefficients $f_{aA\sigma i}$ and of the nuclear coordinates $\{\vec{R}\}$, that is,

$$E = E[f_{aA\sigma i}, \{\vec{R}\}] . \quad (15)$$

Equation (3) for the present HF approach becomes

$$L = e^{\gamma t/2} \left\{ \sum_a \sum_A \sum_\sigma \sum_i \frac{1}{2} m_{aA\sigma i} \dot{f}_{aA\sigma i}^2 \right.$$
$$\left. + \sum_A \frac{1}{2} M_A \dot{\vec{R}}_A^2 - E[f_{aA\sigma i}, \{\vec{R}\}] \right\} . \quad (16)$$

The equations of motion (EM) are obtained from the Lagrangean (16) subjected to the orthonormality constraints

$$\langle \psi_a | \psi_b \rangle = \delta_{ab} . \quad (17)$$

The EM for the expansion coefficients are

$$m_{aA\sigma i} \left(\ddot{f}_{aA\sigma i} + \frac{1}{2} \gamma \dot{f}_{aA\sigma i} \right) + \frac{\partial E}{\partial f_{aA\sigma i}}$$

$$-4 \sum_{a,b} \epsilon_{a,b} \langle \frac{\partial \psi_a}{\partial f_{aA\sigma i}} | \psi_b \rangle = 0 . \quad (18)$$

The last term in (18) is the reaction force due to the constraints (17). If we use the fact that ψ is linear in f, the reaction force becomes

$$-4 \sum_b \sum_B \sum_\rho \epsilon_{ab} \sum_j f_{aB\rho j} S_{\sigma A \rho B}^{i,j} \quad (19)$$

where the overlap matrix is defined by

$$S_{\sigma A \rho B}^{i,j} + \langle \phi_\sigma(\alpha_i, \vec{r}_A) | \phi_\rho(\alpha_j, \vec{r}_B) \rangle . \quad (20)$$

The force related to the linear coefficient $f_{aA\sigma i}$ becomes, after some manipulations,

$$- \frac{\partial E}{\partial f_{aA\sigma i}} = -4 \sum_B \sum_\rho \sum_j f_{aB\rho j} F_{\sigma A \rho B}^{i,j} , \quad (21)$$

where the Fock matrix is given by

$$F_{\sigma A \rho B}^{i,j} \langle \phi_\sigma(\alpha_i, \vec{r}_A) | \hat{F} | \phi_\rho(\alpha_j, \vec{r}_B) \rangle , \quad (22)$$

where F is the usual Fock operator[9]. For $t \to \infty$, the two first terms in (18) vanish. In such conditions, (18-21) lead, after diagonalization of ϵ_{ab}, to

$$\sum_B \sum_\rho \sum_j f_{aB\rho j} \left(F_{\sigma A \rho B}^{i,j} - \epsilon_a S_{\sigma A \rho B}^{i,j} \right) = 0 . \quad (23)$$

This is nothing but the secular equation for the Fock matrix (or Roothaan-HF equations[10]) obeyed by the coefficients $f_{aA\sigma i}$ after convergence. The EM for the nuclei are

$$M_A \ddot{\vec{R}}_A + \frac{1}{2} \gamma \dot{\vec{R}}_A + \vec{\nabla}_A E = 0 . \quad (24)$$

We have $m = N/2$ equations like (18) and Q equations like (24). These two sets of EM shall be integrated simultaneously until a given convergence criterium is reached. At this point, the nuclei will be at their equilibrium position and the orbitals will satisfy the HFR equations.

As in the DFT case, the actual dynamics of the nuclei can be obtained if we neglect the dissipative term in (24) and M_A are the actual nuclear masses. Such a simulation has been made by Hartke an Carter[5a].

That calculation, however, neglects sizeable corrections to He-Fe forces and can only be considered qualitative.

V. Solution of the equations of motion

To solve the EM (18) and (24) we follow the procedure detailed in [4] and sketched below. First, we rewrite the EM as

$$m_k \ddot{q}_k + \frac{1}{2} m_k \gamma \dot{q}_k = f_k \ , \qquad (25)$$

where f_k is the sum of all forces over q_k other than the dissipative one. For example, the force f_k over a coefficient $f_{aA\sigma i} \equiv q_k$ is

$$f_k = -2 \sum_b \left(\langle \frac{\partial \psi_b}{\partial q_k} | \hat{F} | \psi_b \rangle - \epsilon_j \langle \frac{\partial \psi_b}{\partial q_k} | \psi_b \rangle \right) \ , \qquad (26)$$

with

$$\epsilon_b = \langle \psi_b | \hat{F} | \psi_b \rangle \ . \qquad (27)$$

The EM (25) can be integrated with any algorithm suitable for Newtonian equations[11]. In Refs. [3,4] we used the simplest one, namely the Verlet algorithm. The masses m_k are ficticious, and are chosen to correspond approximately to the critical damping condition of a damped harmonic oscillator,

$$m_k \approx -\frac{1}{\gamma^2} \frac{\partial f_k}{\partial q_k} \ . \qquad (28)$$

The EM (25) gives, for each time step At, new values for q_k. With these values, we update the Fock operator F and build a new set of forces f_k. We found that we can save computational time if we keep the $\hat{F}$ frozen during a number of time steps (multistep algorithm)[3].

The solution presented above is refered to as "simulated annealing", SA. Another approach is the "simulated quenching" algorithm SQ, where we neglect the first term in (25) and solve

$$\dot{q}_k = \frac{2f_k}{m_k \gamma} \ , \qquad (29)$$

$$m_k \approx -\frac{2\Delta t}{\gamma} \left(\frac{\partial f_k}{\partial q_k} \right) \ .$$

In both approaches, the initial conditions are $\dot{q}_k = 0$ and q_k obtained from the "bare" hamiltonian (that is, neglecting the electronic repulsion).

As we solve the EM just for the occupied orbitals, the CP approach described above should save a considerable amount of computational time as compared to the SCF procedure. However, as our basis sets are not orthogonal, we might have to handle with the problem of approximate linear dependence (ALD), that is, different sets of $\{q_k\}$ might lead to similar $\psi(\vec{r})$. To solve this problem, we orthogonalize the original basis set $\{\psi_\sigma(\alpha_i, \vec{r}_A)\}$ canonically. This implies on loosing part of the computational gain of the CP procedure, since the orthogonalization is a costly procedure. On the other hand, the method shows great stability and converges in a smaller number of iterations as compared to the SCF procedure, specially for "pathological" systems such as the HF molecule (see Table I). The net result is a method more economical than the SCF method[3].

Table I - Comparison of the number of iterations of HF-MD (SA dynamics) and HF-SCF for systems that present unstability.

System	Method	Iterations	Energy(a.u.)
FH	HF-MD	14	-100.024899
FH	HF-SCF	25	-100.024897

For the simultaneous optimization of wavefunction and geometry (of diatomic molecules), we have found that it is more appropriate to use the SA dynamics for the forrner and the SQ dynamics for the latter. This assures a fast and stable convergence. An additional recipe is used to estimate the (ficticious) nuclei masses. We use

$$\frac{\partial^2 E}{\partial R_A^2} \approx \partial^2 \partial R_A^2 \sum_{A,B} \frac{Z_A Z_B}{R_{AB}} \qquad (30)$$

for the first iteration. For the subsequent iterations, a simple numeric derivative $\Delta/\Delta R$ gives enough precision for our purposes.

After each step in the solution of the EM for the nuclei, we let the wave-function adapt itself to the geometry in order to have a reliable evaluation of the He-Fe forces. Then, the nuclear coordinates are extrapolated along the direction given by the He-Fe forces. To obtain the equilibrium geometry in the fastest way, we let the

Table II - Geometry optimization by HF-MD. All quantities are in a.u. $R_{e,}$ and R_{op} are, respectively, the experimental and the optimized nuclear distances. $E(R_{ex})$ and $E(R_{op})$ are the corresponding energies. N_{st} is the number of steps in the solution of the EM for the nuclei.

System	R_{ex}	$E(R_{ex})$	R_{op}	$E(R_{op})$	N_{st}
H_2	1.400	-1.13289878	1.388	-1.13292909	1
LiH	3.015	-7.98418005	3.026	-7.98418415	1
Li_2	5.051	-14.87044768	5.289	-14.87082640	2

energy converge to an accuracy of 10^{-8} a.u. This assures an accuracy of 10^{-4} a.u. for the He-Fe forces and a very fast convergence to the minimum. Table II shows results for small diatomic molecules starting from the experimental equilibrium distance. The accuracy and the number of iterations are about the same as those obtained with the standard GAUSSIAN program[12] with the same basis set.

Although the method has only been applied so far to diatomic molecules, the extension to polyatomic molecules is straightforward. In this case, the geometry optimization can be obtained with a direction-set method such as the conjugate gradient method[11]. The line minimization along a given direction is performed exactly as in the case of the diatomic molecule.

VI. Molecular dynamics in the Valence Bond approach

In order to have a good description of atomic and molecular interactions for a large range of distances we must go beyond the Hartree-Fock approximation, since it fails to describe molecular dissociation properly. It is necessary, therefore, to include electron correlation from start (not as a perturbation).

One of the methods that include electron correlation (from start) is the Valence Bond (VB) approach. The VB approach can be seen as a configuration interaction (CI) method with chemical insight. Starting from localized atomic orbitals, we form the many-body wavefunction as a linear combination of covalent and ionic structures representing the possible ways that bonds can occur in a molecule. Each structure is an antisymmetrized many-electron function times a spin eigenfunction.

In order to two valence electrons be paired, making a chemical bond, the atomic orbitals occupied by these electrons must overlap, that is, they must be nonorthogonal. This is the major drawback of the VB method, and this is the reason why the VB method has been seldom used up to recent years, if compared to molecular-orbital (MO) methods.

For a two-electron system (the H_2 molecule, for instance), the covalent VB wavefunction is

$$\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1) , \qquad (31)$$

where ϕ_A and ϕ_B are localized non-orthogonal atomic orbitals, centered at nuclei A and B. It gives a correct description of the dissociation of H_2 in two H atoms. If, for a many-electron system, each valence electron singlet pair (a chemical bond) is allowed to occupy a function like (30), and the orbitals are optimized self-consistently, the resulting anti-symmetrized wavefunction is referred to as Generalized Valence Bond (GVB)[13]. Therefore, in the GVB method the electrons are correlated by pairs and we can say that the method is "VB by pairs".

In most cases other approximations are made. It is computationally useful to require that all orbitals other than the two occupied by the singlet pairs are orthogonal. This orthogonality condition is a restriction on the wavefunction. Also, it is common to couple as many orbital pairs as possible for a given spin eigenstate, a procedure referred to as perfect-pairing (PP), giving rise to the GVB-PP method.

The GVB-PP method is useful in many cases but it is inappropriate for systems such as benzene, in which we have two bonding schemes of comparable impor-

tance, as well as for describing the dissociation of systems, such as O_2, that lead to triplet or higher spin states for the fragments.

The GVB-PP approach was recently applied by Hartke and Carter[5b] to describe the formation of the Na_4 cluster within the MD scheme. In that calculation, four valence electrons were coupled in two singlet pairs. To our knowledge, this is the only application of a correlation method (beyond HF) within the CP-MD approach.

Our group has developed a CP-MD method within the valence bond formalism not restricted to the GVB-PP approximation. In this method one can include, in principle, as many structures as desired, and handle any kind of molecular system[14]. To do this we started from the VB approach by McWeeny[15], who developed algorithms for the calculation of matrix elements between nonorthogonal atomic orbitals. In the following, we will describe our VB-MD approach.

We consider the many-electron wavefunction Ψ as a linear combination of structures,

$$\Psi = \sum_{\kappa} C_{\kappa} \Phi_{\kappa} \ , \tag{32}$$

where each structure is of the form

$$\Phi_{\kappa} = \hat{A} \psi_{\kappa_1} \psi_{\kappa_2} ... \psi_{\kappa_n} \Theta \ , \tag{33}$$

where $\hat{A}$ is the antisyrnmetrizing operator, ψ_{κ_i} are localized nonorthogonal atomic orbitals, and O is the total spin eigenfunction. We adopt Φ_1 as a reference structure and assume that the atomic orbitals that appear in the other structures have to appear in the referente structure. Expanding these atomic orbitals in a nonorthogonal basis set $\{\phi_{\mu}\}$,

$$\psi_{\kappa_i} \equiv \psi_i = \sum_{\mu} c_{\mu i} \phi_{\mu} \ , \tag{34}$$

the total energy becomes the functional

$$E = E[\{c_{\mu i}\}, \{C_{\kappa}\}], \tag{35}$$

with which we build the Lagrangean

$$L = e^{\gamma t/2} \left\{ \sum_{\mu,i} \frac{1}{2} m_{\mu i} \dot{c}_{\mu i}^2 + \sum_{\kappa} \frac{1}{2} m_{\kappa} \dot{C}_{\kappa}^2 - E[\{c_{\mu i}\}, \{C_{\kappa}\}] \right\} \tag{36}$$

The EM for the two sets of parameters $\{c_{\mu i}\}$ and $\{C_{\kappa}\}$ are

$$m_{\mu i} \left(\ddot{c}_{\mu i} + \frac{1}{2} \gamma \dot{c}_{\mu i} \right) + \frac{\partial E}{\partial c_{\mu i}} = 0 \tag{37}$$

and

$$m_{\kappa} \left(\ddot{C}_{\kappa} + \frac{1}{2} \gamma \dot{C}_{\kappa} \right) + \frac{\partial E}{\partial C_{\kappa}} = 0 \tag{38}$$

Let us now obtain the expressions for the forces and the ficticious masses. The total energy can be written as

$$E = \frac{\sum_{\kappa,L} C_{\kappa} C_L \langle \Phi_{\kappa} | H | \Phi_L \rangle}{\sum_{\kappa,L} C_{\kappa} C_L \langle \Phi_{\kappa} | \Phi_L \rangle} = \frac{\sum_{\kappa,L} C_{\kappa} C_L S_{\kappa L}}{\sum_{\kappa,L} C_{\kappa} C_L S_{\kappa L}} \ , \tag{39}$$

so that the forces associates to the C, are

$$\frac{\partial E}{\partial C_\kappa} = \frac{2\sum_L C_L(H_{\kappa L} - ES_{\kappa L})}{\sum_{\kappa',L} C_\kappa C_L S_{\kappa',L}} \ . \qquad (40)$$

To calculate the forces associated to the $c_{\mu i}$, we write the general expression

$$\delta E = \frac{2\langle\Psi|H - E|\delta\Psi\rangle}{\langle\Psi|\Psi\rangle} \ , \qquad (41)$$

so that we only need the derivatives of Ψ related to the $c_{\mu i}$. We have

$$\frac{\partial\Psi}{\partial c_{\mu i}} = \sum_\kappa \hat{A}\frac{\partial}{\partial c_{\mu i}}(\psi_{\kappa_1}\psi_{\kappa_2}...\psi_{\kappa_n})\Theta \ . \qquad (42)$$

For an arbitrary structure where the orbital ψ_i appears, we have

$$\frac{\partial\Phi_\kappa}{\partial c_{\mu i}} = \hat{A}(\psi_{\kappa_1}\psi_{\kappa_2}...\frac{\partial\psi_{\kappa_i}}{\partial c_{\mu i}}...\psi_{\kappa_n})\Theta \ . \qquad (43)$$

In view of (33), we have

$$\frac{\partial\Phi_\kappa}{\partial c_{\mu i}} = \hat{A}(\psi_{\kappa_1}\psi_{\kappa_2}...\phi_\mu...\psi_{\kappa_n})\Theta = \Phi_\kappa^{\mu i} \ . \qquad (44)$$

That is, the effect of the operator $\partial/\partial c_{\mu i}$ is to generate a new structure $\Phi_\kappa^{\mu i}$ where the orbital ψ_i is replaced by the basis function ϕ_μ. We can write

$$\frac{\partial\Psi}{\partial c_{\mu i}} = \sum_\kappa C_\kappa \frac{\partial}{\partial c_{\mu i}}\Phi_\kappa \equiv \Psi^{\mu i} \ , \qquad (45)$$

and the forces related to the coefficients $c_{\mu i}$ are

$$\frac{\partial E}{\partial c_{\mu i}} = \frac{2\langle\Psi|H - E|\Psi^{\mu i}\rangle}{\langle\Psi|\Psi\rangle} \qquad (46)$$

The ficticious masses related to the coefficients are taken as approximately proportional to the second derivative of the total energy. We use

$$m_\kappa = \frac{2(H_{\kappa\kappa} - ES_{\kappa\kappa})}{\sum_{\kappa',\lambda} S_{\kappa'\lambda}} \ , \qquad (47a)$$

$$m_{\mu i} = \frac{2\langle\Psi^{\mu i}|H - E|\Psi^{\mu i}\rangle - 4\frac{\partial}{\partial c_{\mu i}}\langle\Psi|\Psi^{\mu i}\rangle}{\langle\Psi|\Psi\rangle} \ . \qquad (47b)$$

Now, identifying the set of parameters C, and $c_{\mu i}$ with a set of generalized coordinates q_k, with forces $f_k = -\partial E/\partial q_k$, we solve the EM with the same SQ algorithm described in the previous section, that is, we iterate the equations

$$q_k(t + \nabla t) = q_k(t) + \alpha\frac{f_k}{m_k} \ , \qquad (48)$$

where a is a constant, until the forces vanish within a given convergence criterion. To speed up the convergence, we also use the numerical extrapolation technique DIIS - direct inversion of iterative subspace[16].

We have performed tests for the above algorithm on the H_2O and CH_4 molecules. Convergence on the the total energy at the level of 10^{-6} a.u. was obtained with 68 iterations for H_2O, and 48 iterations for CH_4. Simultaneous optimization of the wavefunction and geometry of some systems of interest is in progress.

VII. Concluding remarks

The CP-MD approach opened the possibility of simulating the dynamical behavior of molecular and condensed matter systems from first principles. We have shown that the CP-MD method, although primarily designed for DFT calculations, can be extended to quantum chemistry calculations either at the HF level or at a CI level (VB approach). The HF-MD and the VB-MD methods described here can be applied to a wide range of quantum chemistry problem, such as geometry optimization of complex molecules or the dynamics of chemical reaction and cluster formation. The VB-MD method can also be applied to condensed matter problems where electron correlation is important, such as deep levels in semiconductors and insulators.

Acknowledgments

References

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

2. M. R. Pederson, B. M. Klein and J. Q. Broughton, Phys. Rev. B 38, 3825 (1988); D. Hohl, R. O. Jones, R. Car and M. Parrinello, J. Chem. Phys. 89, 6823 (1988); J. Harris and D. Hohl, J. Phys: Condensed Matter 2, 5161 (1990); N. Binggeli, J. L. Martins and J. R. Chelikowsky, Phys. Rev.

Lett. 68, 2956 (1992). See also: B. Feuston, C. Lee and E. Clementi, in MOTECC - Modern *Techniques* in *Computational* Chemistry, edited by E. Clementi (ESCOM, Leiden, 1991).

3. H. Chacham and J. R. Mohallem, Mol. Phys. **70,** 391 (1990).

4. R. O. Vianna, H. Chacham and J. R. Mohallein, J. Chem. Phys. **98,** 6395 (1993).

5. (a) B. Hartke and E. A. Carter, Chem. Phys. Lett. 189, 358 (1992); (b) ibid, J. Chem. Phys. 97, 6569 (1992).

6. R. O. Vianna, R. Custodio, H. Chacham and J. R. Mohallem, Int. J. Quantum Chem. Symp. 26, 311 (1992).

7. P. C. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

8. W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

9. D. R. Hartree, The *Calculation of Atomic* Structures (Wiley, New York, 1957).

10. C. C. J. Roothaan, Rev. Mod. Phys. **23,** 69 (1951).

11. W. H. Press, B. P. Flannery, S. A. Tenkolsky and W. T. Vetterling, Numerical Recipes (Cambridge Univ. Press, Cambridge, 1986).

12. GAUSSIAN92, Revision B, Gaussian Inc., Pittsburgh, PA, 1992.

13. F. W. Bobrowicz and W. A. Goddard III, in Methods of Electronic Structure Theory, edited by H. F. Schaeffer (Plenum, New York, 1977).

14. R. O. Vianna, J. R. Mohallem, and R. McWeeny, in preparation.

15. R. McWeeny, J. Mol. Structure 229, 29 (1991).

16. P. Pulay, Chem Phys. Lett. 73, 393 (1980); T. P. Hamilton and P. Pulay, J. Chem. Phys. 84, 5728 (1986).