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Constrained mechanics for the dynamical simulated annealing of Coulomb systems

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Summary. The energy expression for many-electron systems is rewritten by applying a Gaussian transformation to the two-body matrix elements of the Coulomb interaction. The resulting field theory is treated as a classical dynamical system leading to a set of equations of motion. This treatment of the quantum many-particle problem allows for a common formulation of *ab initio* Molecular Dynamics simulations and the microcanonical approach to lattice field theories. Solution of the Hartree-Fock equations or optimization of the single particle basis used in a configuration interaction expansion can be obtained by the method within an *ab initio* Molecular Dynamics framework.

Key words: *Ab initio* Molecular Dynamics – Many-Electron theory – Optimization

1 Introduction

The method of simulated annealing has proven to be a powerful tool for minimization problems [1]. For atomic and molecular systems, the method of dynamical simulated annealing was introduced [2]: a classical dynamics for the nuclear coordinates and any external parameters is introduced as well as for the electronic degrees of freedom. In this approach, the electronic wave functions are treated as dynamical variables satisfying a fictive equation of motion. Minimization of the total energy is then achieved by rescaling of the "velocities" until the system is trapped into a local minimum of the energy surface; hence the name dynamical simulated annealing. The dynamical simulated annealing of Car and Parrinello [2] is presented in context of the density functional expression for the total energy [3]. A similar strategy is given here for the solution of the Hartree–Fock equations or for optimization of one electron functions used in a configuration interaction (CI) in a way similar to multiconfiguration self consistent field (MCSCF) methods. No matrix diagonalizations are required for the solution of the mean field equations or for the determination of the optimal basis functions.

To make contact with a method common to problems in field theory [4, 5], the energy expectation value is rewitten with the aid of a Gaussian transformation that is similar in approach to the Hubbard–Stratonovich transformation [6, 7]. However, the Hubbard–Stratonovich transformation is an operator identity.

By applying a Gaussian transformation directly to the two-body expectation values of the Coulomb problem, a classical field theory is achieved and is directly accessible to a classical dynamics interpretation.

2 The Hubbard–Stratonovich transformation

By writing two-body interactions in an explicitly quadratic form, the Hubbard–Stratonovich (H–S) transformation makes use of Gaussian integrals to rewrite the two-body terms as functional integrals over a one-body potential. The transformation is an operator identity and relies on the second quantization formulism. In many-fermion problems, second quantization is the operator version of expressing a state as an infinite sum over Slater determinants built up from a complete single particle basis. As such, the second quantization formulation of the problem is equivalent to the configuration interaction (CI) expansion with which creation and destruction operators are not necessarily introduced. The operator formulation of the H–S transformation is reviewed in this section. A similar transformation is applied in the following section directly to symmetric two-body matrix elements without relying on the second quantization method.

The H–S transformation can be applied to a Hamiltonian consisting of one-body and two-body interactions:

$$\begin{aligned}\hat{H}(1,2,\cdots,n)&=\sum_i \hat{h}_i+\tfrac{1}{2}\sum_{ijkl}\hat{V}_{ij;kl}\\&=\hat{H}^{(1)}+\hat{H}^{(2)},\end{aligned} \tag{1}$$

where

$$\begin{aligned}\hat{h}_i&=\varepsilon_i\hat{a}_i^\dagger\hat{a}_i,\\ \hat{V}_{ij;kl}&=v_{ij;kl}\hat{a}_i^\dagger\hat{a}_j\hat{a}_k^\dagger\hat{a}_l.\end{aligned} \tag{2}$$

The H–S transformation is usually applied to the partition function

$$Z=\mathrm{Tr}\exp\left[-\beta\hat{H}^{(1)}-\beta\hat{H}^{(2)}\right], \tag{3}$$

with $\beta=1/kT$ the inverse temperature. Due to the noncommutativity of $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$, the partition function is rewritten

$$\begin{aligned}Z&=\mathrm{Tr}\exp\left[-\sum_m s(\hat{H}^{(1)}+\hat{H}^{(2)})\right]\\&\approx\mathrm{Tr}\lim_{m\to\infty}\prod_m\exp[-s\hat{H}^{(1)}]\exp[-s\hat{H}^{(2)}],\end{aligned} \tag{4}$$

with $s=\beta/m$ the Trotter time. As $m\to\infty$, Eq. (4) becomes accurate to order $\mathcal{O}(s^2)$. The H–S transformation relies on a symmetric interaction

$$v_{ij;kl}=v_{kl;ij}. \tag{5}$$

The two-body interactions are then quadratic and may be written with aid of the Gaussian integral

$$\exp(\tfrac{1}{2}x^2)=\int\frac{d\phi}{\sqrt{2\pi}}\exp(-\tfrac{1}{2}\phi^2+x\phi) \tag{6}$$

as

$$\exp\left[-\tfrac{1}{2}s\sum_{ij} v_{ij;kl}\hat{a}_i^\dagger \hat{a}_j \hat{a}_k^\dagger \hat{a}_l\right] \approx \int \sqrt{\frac{s}{2\pi}}\,\Pi\,\mathrm{d}\phi_{ij}\exp\left[-\tfrac{1}{2}s\sum_{ij}\phi_{ij}^2 + \mathrm{i}s\sum_{ij}\phi_{ij}v_{ij;ij}^{1/2}\hat{a}_i^\dagger \hat{a}_j\right] \tag{7}$$

after transforming $v_{ij;kl}$ to diagonal form. Equation (7) is the essence of the H–S transformation: the two-body terms on the left hand side are expressed as Gaussian integrals over a single-body interaction. Substitution of Eq. (7) into the complete expression for the partition function Eq. (4) completes the transformation. Expansion of the exponential of the term linear in ϕ and applying Wick's theorem to the time development operator $Z[\beta = \mathrm{i}t] = U(t, 0)$ allows for a diagrammatic expansion of the complete many-body problem. Expanding about different stationary points allows for a straightforward determination of various forms of the Many-Body Perturbation Theory (MBPT) expansion [7, 8].

3 A Gaussian transformation for the matrix elements of symmetric two-body interactions

A similar derivation will now be given for the two-body terms of a CI expansion. This functional mimic of the H–S transformation is given for fermion systems in three spatial dimensions and a real, symmetric potential: in particular, the Coulomb interaction. However, the discussion is sufficiently flexible to be applicable to other potentials as well as boson systems.

The n-particle Hamiltonian takes the form:

$$\begin{aligned}\hat{H}(1,2,\cdots,n) &= \sum_{i=1}^{n} h(x_i) + \tfrac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{n} V(x_i, x_j)\\ &= \hat{H}^{(1)} + \hat{H}^{(2)}.\end{aligned} \tag{8}$$

with

$$h(x) = -\tfrac{1}{2}\nabla_x^2 + V(x), \tag{9}$$

the sum of the kinetic energy and any one-body potentials. The basic quantity to be considered will be the expectation value of the Hamiltonian operator

$$E = \langle \Psi(1,2,\cdots,n)|\hat{H}|\Psi(1,2,\cdots,n)\rangle \tag{10}$$

(throughout the following, volume elements are implied to contain spin products). Any state of many-body system may be represented as a CI expansion:

$$|\Psi(1,2,\cdots,n)\rangle = \sum_A c_A|\Psi_A\rangle, \tag{11}$$

where Ψ_A is a single configuration state function (CSF). The CSFs are the spin coupled sums of Slater determinants built-up from a complete set of single particle functions ψ_i and i labels a set of quantum numbers for a single particle state. The single particle functions are assumed to be orthogonal and normalized:

$$\langle\psi_i|\psi_j\rangle = \delta_{ij}. \tag{12}$$

For the Hamiltonian Eq. (8), the expectation values may be written in terms of the first and second order density matrices. In particular for the two-body terms, the expectation value becomes

$$\langle\Psi|\hat{H}^{(2)}|\Psi\rangle=\int d^3x_1\, d^3x_2\, V(x_1,x_2)\Gamma(x_1,x_2|x_1,x_2), \tag{13}$$

with

$$\Gamma(x_1',x_2'|x_1,x_2)=\binom{n}{2}\int d^3x_3\cdots d^3x_n\Psi^*(x_1',x_2',\cdots,x_n)\,\Psi(x_1,x_2,\cdots,x_n). \tag{14}$$

It is convenient to consider a truncated CI expansion whereby the single particle basis is restricted to M expansion functions: this allows the problem to be formulted in terms of finite matrices. The final result may be made arbitrarily accurate by allowing M to become as large as required. With help of the CI expansion, the second order density matrix is rewritten

$$\Gamma(x_1',x_2'|x_1,x_2)=\binom{n}{2}\sum_{A,B}c_{A}^{*}c_{B}\int d^3x_3\cdots d^3x_n \times\Psi_A^*(x_1',x_2',\cdots,x_n)\,\Psi_B(x_1,x_2,\cdots,x_n). \tag{15}$$

The two-body terms can be written

$$\langle\Psi|\hat{H}^{(2)}|\Psi\rangle=\int d^3x_1\, d^3x_2\, \rho(x_1,x_1)\Gamma V(x_1,x_2)\rho(x_2,x_2) \tag{16}$$

with

$$\begin{aligned}\rho(x,y)=(&\rho_{11}(x,y),\quad \rho_{12}(x,y),\cdots,\rho_{1M}(x,y),\\ &\rho_{21}(x,y),\quad \rho_{22}(x,y),\cdots,\rho_{2M}(x,y),\cdots,\\ &\rho_{M1}(x,y),\quad \rho_{M2}(x,y),\cdots,\rho_{MM}(x,y)).\end{aligned} \tag{17}$$

and

$$\rho_{ij}(x,y)=\psi_i^*(x)\psi_j(y). \tag{18}$$

Γ is the $M^2\times M^2$ symmetrized matrix of the coefficients of each of the terms $\rho_{ij}(x,x)\rho_{kl}(y,y)$arising from Eq. (15). The matrix Γ may be transformed to diagonal form

$$\Gamma_{\alpha\alpha}'=\sum_{\beta\gamma}U_{\alpha\beta}\Gamma_{\beta\gamma}U_{\gamma\delta}^{\dagger} \tag{19}$$

resulting in the new vectors

$$\rho_\beta'(x,x)=\sum_\alpha\rho_\alpha(x,x)\,U_{\alpha\beta}. \tag{20}$$

A Greek subscript is being used to denote a two-particle state $\alpha=(ij)$. Whereas natural orbitals [9] are the product orbitals that diagonalize the first order density matrix, the transformation Eq. (19) relies on the product-orbitals which diagonalize the second order density matrix. In diagonal form, the two-body expectation value becomes

$$\langle\Psi|\hat{H}^{(2)}|\Psi\rangle=\sum_{\alpha}\Gamma'_{\alpha\alpha}\int \mathrm{d}^3x_1\,\mathrm{d}^3x_2\,\rho'_\alpha(x_1,x_1)V(x_1,x_2)\rho'_\alpha(x_2,x_2). \tag{21}$$

The square root of the interaction may be defined as follows:

$$V(x,y)=\int \mathrm{d}^3x'\,\mathscr{V}^{1/2}(x,x')\mathscr{V}^{1/2}(x',y). \tag{22}$$

Equations (19) and (22) allow the interaction matrix elements to be written explicitly quadratic

$$\langle\Psi|\hat{H}^{(2)}|\Psi\rangle=\sum_{\alpha}\Gamma'_{\alpha\alpha}\int \mathrm{d}^3x\left(\int \mathrm{d}^3y\,\mathscr{V}^{1/2}(x,y)\rho'_\alpha(y,y)\right)^2. \tag{23}$$

A discrete approximation to the outer integration results in

$$\langle\Psi|\hat{H}^{(2)}|\Psi\rangle=\sum_{\alpha}\Gamma'_{\alpha\alpha}\sum_{j}(v_\alpha^{1/2}(x_j))^2, \tag{24}$$

where the function

$$v_\alpha^{1/2}(x_j)=\int \mathrm{d}^3y\,\mathscr{V}^{1/2}(x_j,y)\rho'_\alpha(y,y) \tag{25}$$

has been implicitly averaged over cells of volume δ^3x. The cells are then replaced with a lattice of points Z^3 and to each lattice point there is assigned a value $v_\alpha^{1/2}(x_j)$.

The energy expectation value may be exponentiated and written simply as

$$\mathrm{e}^{\beta E}=\mathrm{e}^{\beta\langle\Psi|\hat{H}^{(1)}|\Psi\rangle}\mathrm{e}^{\beta\langle\Psi|\hat{H}^{(2)}|\Psi\rangle}, \tag{26}$$

since the expectation values are scalars and therefore commute. Again using Eq. (6), a Gaussian variable is introduced at each lattice point

$$\exp[\beta\langle\Psi|\hat{H}^{(2)}|\Psi\rangle]=\int\prod_{\alpha,j}\left[\sqrt{\frac{\beta\Gamma'_{\alpha\alpha}}{\pi}}\,\mathrm{d}\phi_\alpha(x_j)\right]$$
$$\times\exp\left[-\sum_{\alpha}\beta\Gamma'_{\alpha\alpha}\int \mathrm{d}^3x\,\phi_\alpha^2(x)+2\sum_{\alpha}\beta\Gamma'_{\alpha\alpha}\int \mathrm{d}^3x\,\phi_\alpha(x)v_\alpha^{1/2}(x)\right]. \tag{27}$$

Equation (27) is the form corresponding to Eq. (7). Whereas Eq. (7) applies to the n-particle Hamiltonian written in second quantized form, Eq. (27) is valid for two-body matrix elements (scalar) terms. While formally similar, the two transformations have notable differences. Firstly, there is no Trotter time (the parameter s in Eq. (4)) in the functional version of the transformation. Secondly, Fermi statistics in the operator version are preserved through the operators $\hat{a}_i^\dagger\hat{a}_j$ whereas the result of Fermi statistics is contained within the density coefficients $\Gamma_{\alpha\beta}$ for the functional form.

A functional change of variables may be introduced as follows:

$$\int \mathrm{d}^3x\,\mathscr{V}^{1/2}(x,y)\phi_\alpha(x)=\phi'_\alpha(y). \tag{28}$$

The two-body terms becomes

$$\exp[\beta\langle\Psi|\hat{H}^{(2)}|\Psi\rangle]=\mathscr{J}\int\mathscr{D}\phi'\exp\left[-\beta\sum_{\alpha}\Gamma'_{\alpha\alpha}\int d^3x\,\phi'_\alpha(x)\hat{V}^{-1}\phi'_\alpha(x)\right.$$
$$\left.+2\beta\sum_{\alpha}\Gamma'_{\alpha\alpha}\int d^3x\,\phi'_\alpha(x)\rho'_\alpha(x,x)\right] \tag{29}$$

where $\mathscr{J}$ is the Jacobian for the change of variable Eq. (28) (in this case, the Fredholm determinant $\det(\hat{V}^{-1/2})$). The operator $\hat{V}^{-1}$ is defined by

$$\hat{V}^{-1}V(x,y)=\delta^3(x-y) \tag{30}$$

given explicitly for the Coulomb interaction as

$$\hat{V}^{-1}=-\frac{1}{4\pi}\nabla_x^2. \tag{31}$$

The second order density matrix may be returned to non-diagonal form

$$\exp[\beta\langle\Psi|\hat{H}^{(2)}|\Psi\rangle]=\int\mathscr{D}\phi\exp\left[-\beta\sum_{\alpha,\beta}\Gamma_{\alpha\beta}\int d^3x\,\phi_\alpha(x)\hat{V}^{-1}\phi_\beta(x)\right.$$
$$\left.+2\beta\sum_{\alpha\beta}\Gamma_{\alpha\beta}\int d^3x\,\phi_\alpha(x)\rho_\beta(x,x)\right]. \tag{32}$$

As for the H–S transformation [7], the stationary point of the functional integral is given by the Hartree mean field which is the Coulomb potential due to a classical charge distribution:

$$\phi_\alpha^0(x)=\int d^3y\,V(x,y)\rho_\alpha(y,y). \tag{33}$$

Using the functional form of the transformation, the total energy can be put in the form

$$e^{\beta E}=\int\mathscr{D}\phi\exp\left[\beta\int d^3x\,\mathscr{E}[\phi,\psi^*,\psi]\right], \tag{34}$$

with

$$\mathscr{E}(x)=\sum_{ij}\psi_i^*(x)\left\{\gamma_{ij}[-\tfrac{1}{2}\nabla^2+V(x)]+2\sum_{kl}\Gamma_{ijkl}\phi_{kl}(x)\right\}\psi_j(x)$$
$$-\sum_{ijkl}\phi_{ij}(x)\Gamma_{ijkl}\hat{V}^{-1}\phi_{kl}(x). \tag{35}$$

When the stationary condition is fulfilled, the total energy is

$$E=\sum_{ij}\langle\psi_i|\mathscr{H}_{ij}[\phi^0]|\psi_j\rangle-\sum_{ijkl}\Gamma_{ijkl}\langle\psi_i\psi_k|\hat{V}|\psi_j\psi_l\rangle, \tag{36}$$

with

$$\mathscr{H}_{ij}[\phi^0]=\gamma_{ij}[-\tfrac{1}{2}\nabla^2+V(x)]+2\sum_{kl}\Gamma_{ijkl}\phi_{kl}^0(x). \tag{37}$$

The first term is the sum of the one-particle energies and the second term corrects the over-counting of the two-body potentials occurring in first sum. If there are $M=n$ expansion functions only one Slater determinant can be constructed. In this case, only the n lowest states are occupied and $\gamma_{ij}=\delta_{ij}$ for $i, j \leqslant n$ and is zero otherwise. Requiring the field ϕ to satisfy the stationary condition results in the standard expression for the energy of the Hamiltonian Eq. (8) in a single Slater determinant:

$$E=\sum_{i=1}^{n} \int \mathrm{d}^3 x \psi_i^*(x)[-\tfrac{1}{2} \nabla^2+V(x)] \psi_i(x) + \tfrac{1}{2} \sum_{i,j=1}^{n} \int \mathrm{d}^3 x \mathrm{d}^3 y \psi_i^*(x) \psi_j^*(y) V(x, y)[\psi_i(x) \psi_j(y)-\psi_i(y) \psi_j(x)]. \tag{38}$$

Clearly, variation of the energy $E[\psi^*, \psi]$ with the constraint of orthogonality of the single particle functions results in the Hartree–Fock equations.

If the energy in Eq. (34) is varied with respect to ψ^* and ψ, the following two equations arise:

$$\sum_j \left\{\gamma_{ij}[-\tfrac{1}{2} \nabla^2+V]+2 \sum_{kl} \Gamma_{ijkl} \phi_{kl}\right\} \psi_j=\sum_j \varepsilon_{ij} \psi_j \tag{39}$$

and

$$\sum_j \left\{\gamma_{ji}[-\tfrac{1}{2} \nabla^2+V]+2 \sum_{kl} \Gamma_{jikl} \phi_{kl}\right\} \psi_j^*=\sum_j \varepsilon_{ij} \psi_j^*, \tag{40}$$

where the Lagrangian multipliers ε_{ij} have been introduced to enforce orthogonality of the single particle functions. If the complex conjugate of Eq. (40) is substracted from Eq. (39), the following condition on the Lagrangian multipliers arises:

$$\sum_j \psi_j(\varepsilon_{ij}-\varepsilon_{ji}^*)=0, \tag{41}$$

where it has been assumed that $\phi_{kl}^*=\phi_{lk}$ which holds for the stationary condition. Since the ψ_j are linearly independent, the Lagrangian multipliers form a Hermitian matrix which can be diagonalized and identified with the single particle energies. In particular, if the conditions on the single particle densities are those appropriate for the single Slater determinant case and the fields satisfy the stationary condition, Eq. (39) with ε diagonal is the set of Hartree–Fock equations:

$$\left[-\tfrac{1}{2} \nabla^2+V\right] \psi_i+2 \sum_{jkl} \Gamma_{ijkl} \phi_{kl}^0 \psi_j=\varepsilon_i \psi_i. \tag{42}$$

4 Minimization dynamics

Often, when given a functional integral of the form

$$Z=\int \mathscr{D} \phi \exp[-S_B[\phi]], \tag{43}$$

it is desired to generate a large number of field configurations to stochastically sample the bosonic action $S_B[\phi]$. Callaway and Rahman [4] made the observation that by defining a Hamiltonian

$$H=\frac{p^2}{2m}+S_B[\phi], \tag{44}$$

with p independent of ϕ does not change the calculation of expectation values

$$\langle F[\phi]\rangle=\int\mathscr{D}\phi F[\phi]\exp[-S_B[\phi]], \tag{45}$$

where $F[\phi]$ is a functional of the fields ϕ. They define a modified functional integral

$$Z=\int\mathscr{D}\phi\,\mathscr{D}p\exp[-H[p,\phi]] \tag{46}$$

and use classical dynamics to generate field configurations ϕ. This microcanonical formulation was then extended to systems containing fermions by Polonyi and Wyld [5]. The Gaussian transformation derived in Section 3 is of the form explicitly considered by Polonyi and Wyld so that a short digression to discuss their method follows.

In their treatment, the action

$$S[\phi,\psi^*,\psi]=\frac{1}{2}\sum_{i,j}\psi_i^*\mathscr{M}_{ij}[\phi]\psi_j+S_B[\phi] \tag{47}$$

is modelled by use of a Hamiltonian system with conjugate variables $\{P_i,Q_i\}$ and $\{p_i,q_i\}$

$$H=\tfrac{1}{2}P_i\mathscr{M}_{ij}^{-1}[q]P_j+\omega^2Q_i^2+\tfrac{1}{2}p_k^2+S_B[q] \tag{48}$$

(note the use of $\mathscr{M}^{-1}$ in defining the Hamiltonian). The Euler–Lagrange equations are given by

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathscr{M}[q]\dot{Q}=-\omega^2Q,$$

$$\ddot{q}=-\delta S_B[q]/\delta q+\frac{\delta}{\delta q}\dot{Q}\mathscr{M}[q]\dot{Q}. \tag{49}$$

Integration of the equations of motion results in phase space points on a constant energy surface and with the usual assumption of ergodicity a microcanical ensemble of states will be generated. In this way, the ficticious dynamics introduced in Eq. (49) are being used to generate field configurations for determining statistical weights needed for calculating expectation values with the functional integral Eq. (45).

The energy density Eq. (35) is seen to be in the form of Eq. (47) through the following identifications:

$$\tfrac{1}{2}\mathscr{M}_{ij}[\phi]=\gamma_{ij}[-\tfrac{1}{2}\nabla^2+V(x)]+2\sum_{kl}\Gamma_{ijkl}\phi_{kl}(x)\equiv\mathscr{H}_{ij}[\phi],$$

$$S_B[\phi]=-\sum_{ijkl}\phi_{ij}(x)\Gamma_{ijkl}\hat{V}^{-1}\phi_{kl}(x). \tag{50}$$

The goal is to minimize the total energy with two constraints:

1. orthogonality of the single particle expansion functions Eq. (12).
2. the fields ϕ_{ij} should satisfy the stationary condition Eq. (33).

Now the purpose of the fictive dynamics is not to generate many sets of field configurations ϕ, ψ^*, ψ to sample many values of the action, rather any dynamics defined should attempt to find the global minimum of the energy functional $E[\phi, \psi^*, \psi]$. To this purpose, the following Lagrangian density is defined:

$$\mathscr{L}(x)=\psi_i^* \mathscr{H}_{ij}[\phi]\psi_j+\tfrac{1}{2}\dot{\phi}_{kl}^2+S_B[\phi]. \tag{51}$$

Note that whereas Polonyi and Wyld chose to introduce a harmonic potential for the P_i momenta, Eq. (51) introduces no corresponding potential. Without loss of generality, in the following ψ^* and ψ will not be treated as independent variables. The Lagrangian for the system then gives rise to the following equations of motion:

$$\begin{aligned}\mathscr{H}[\phi]\dot{\psi}&=-\dot{\mathscr{H}}[\phi]\psi,\\ \ddot{\phi}&=-\delta/\delta\phi\{S_B[\phi]+\psi_i^*\mathscr{H}_{ij}[\phi]\psi_j\}.\end{aligned} \tag{52}$$

The equation of motion for ϕ allows for updating of the fields and insures that when the "forces" $\ddot{\phi}$ are zero, the stationary condition is fulfilled. However, in Eq. (52) there is no means of assuring the orthogonality of the single particle wave functions. Normally when restricting the dynamics of a system, the canonical coordinates Q are subject to constraints: for the dynamics defined by Eq. (52) it is desired to constrain the velociites $\dot{Q}\equiv\psi$. To do this, Lagrangian multipliers are again introduced

$$\delta\int \mathrm{d}t\,\mathrm{d}^3x\,\mathscr{L}=0\rightarrow\delta\int\mathrm{d}t\,\mathrm{d}^3x\left\{\mathscr{L}-\sum_{ij}\psi_i^*\varepsilon_{ij}(t)\psi_j\right\}=0. \tag{53}$$

The constrained equations of motion for the single electron functions become

$$\begin{aligned}(\mathscr{H}[\phi]-\varepsilon)\dot{\psi}&=-(\dot{\mathscr{H}}[\phi]-\dot{\varepsilon})\psi,\\ (\mathscr{H}[\phi]-\varepsilon)\Delta\psi&=-(\Delta\mathscr{H}[\phi]-\Delta\varepsilon)\,\psi,\end{aligned} \tag{54}$$

where in the second form $\mathrm{d}f/\mathrm{d}t$ was replaced by $\Delta f/\Delta t$ and both sides of the equation were multiplied by Δt (if Δ is the forward finite difference operator, Eq. (54) is accurate to first order).

After rather elaborate manipulations, this approach to *ab initio* Molecular Dynamics leads to a simple interpretation: the potentials, not the wave functions, appear to be the natural candidates for a fictive dynamics scheme. Once the potentials ϕ_{ij} have been updated with some integration scheme, the constraint of orthogonality leads directly to the first order $\Delta\mathscr{H}[\phi]$ perturbative correction to the wave functions. The updated "velocities" (single particle functions) are then orthogonal to second order in the perturbation. At the Hartree–Fock solution, any first order corrections to the wave functions vanish [10].

The dynamics defined by Eq. (52) does not allow for an energy loss: there is no quenching process whereby the system becomes trapped in a low energy state. A scaling of the "velocities" until the system has "cooled" can be introduced as in the Car–Parinello method [2]. As an alternative to velocity scaling, a dissipative function can be defined

$$\mathscr{F}=\dot{\phi}_{ij}k_{ijkl}\dot{\phi}_{kl}. \tag{55}$$

The associated non-conservative force

$$F_{\mathscr{F}}=-\delta\mathscr{F}/\delta\phi=-k_{ijkl}\dot{\phi}_{kl} \tag{56}$$

can be added to the equation of motion for the potentials ϕ. By controlling the values of the dissipation constants k, the rate of energy loss can be regulated. Hence, the dynamics consequently becomes a minimization procedure and no rescaling of "velocities" is necessary. By applying the fictitious dynamics to the potentials and truly constraining the wave functions allows for, in the sense that there is no *ad hoc* orthogonolizations of the wave functions and no discontinuous rescaling of velocities, a "smooth" search of the space defined by the energy functional $E[\phi, \psi^*, \psi]$. The concepts of orbital optimization and wave function damping can be expressed directly in terms of the fictive dynamics.

5 Discussion

Car and Parinello [2] write the equation of motion for the electronic wave functions as

$$\mu\ddot{\psi}_i = -\delta/\delta\psi_i E + \sum_j \varepsilon_{ij}\psi_j \tag{57}$$

with the introduction of the "mass" μ. First, it should be noted that the wave functions ψ are playing the role of coordinates as opposed to previous section where the wave functions play the role of velocities. Eq. (57) is then integrated for one "timestep" and the wave functions obtained are no longer orthogonal: some orthogonalization method is then applied to wave functions [2, 11, 12]. The system is then allowed to cool by gradual rescaling of the "velocities" $\dot{\psi}$. In the approach outlined in the previous section, the potentials ϕ_{ij} are integrated for one "timestep". The resulting change in the potentials is then treated as a perturbation to determine the new single particle wave functions: the perturbation correction is the constrained "dynamics" of the one electron wave functions. Energy loss can be introduced by velocity scaling or by dissipative mechanics.

The method outlined here is suitable for Hartree–Fock *ab initio* Molecular Dynamics simulations [13] where the density coefficients γ_{ij} are known and only small corrections to the electron wave functions are necessary due to the movement of the nuclei over a single (physical) timestep. However, the method has been presented to allow its extension to cases where the electronic wave function is represented by a CI expansion. Then, as the nuclei follow a trajectory, the CI expansion coefficients are also changing: the method described can be used for wave function optimization as the new CI vectors are determined as done with MCSCF methods.

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