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On the formalism of many-electron dynamics

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Abstract. The classical Lagrangian governing a system with real nuclear and fictitious 'electronic' degrees of freedom is derived explicitly in the most general case of the choice of parameters such as LCAO coefficients, centres of the basis set orbitals, and multiconfiguration coefficients. 'Electronic' dynamics is in general non-Newtonian. The expressions for the appropriate masses are obtained in the limit of small velocities. The dynamics of nuclei occurs on the Born–Oppenheimer potential energy hypersurface because their equations of motion are determined by the Hellmann–Feynman-type forces becoming dependent upon the 'electronic' coordinates and the corresponding conjugate momenta.

1. Introduction

Since 1985, when Car and Parrinello [1] (see [2–4] for a review) offered the approach now bearing their names, the many-electron molecular dynamics method has been rethought and considerably remodified to treat the electronic and nuclear subsystems on an equal classical mechanics footing. Referring originally to the one-electron density formulation of the quantum many-body variational principle (see [5] for review), the Car–Parrinello approach has been further directly extended to the Hartree–Fock variational principle [6].

In fact, the idea behind this approach is indeed superior. It does not rely on the particular form of the many-body variational principle employed, and it is based on the fact that any trial quantity, say Θ (the one-electron density, ρ, or the many-electron wavefunction, Ψ, for example) involved in either form of the variational principle, should possess, by definition, some parameters α, β, γ, etc. The latter parameters are interpreted as classical degrees of freedom, and the final thing that must be done is to write a classical mechanics Lagrangian governing their dynamics and agreeing with the quantum many-body variational principle, in terms of $E[\Theta]$, for the chosen parental trial quantity Θ. Within the usual Born–Oppenheimer approach, for instance, the procedure of constructing such a Lagrangian mostly concerns the so-called 'electronic' degrees of freedom associated with those trial parameters that were included in Θ, because the nuclear variables are still treated semiclassically, by straightforward analogy with the traditional molecular dynamics method. Such a procedure, aiming at deriving the appropriate equations of motion, must tell us how to determine the quantities that lie at the heart of classical dynamics: the masses corresponding to all degrees of freedom and the forces acting upon them.

The Car–Parrinello Lagrangian deals with all 'electronic' degrees of freedom in a Newtonian manner. Namely, it is a working suggestion that the corresponding masses are just numbers, even originally ignoring their differences, no matter which sort of parametrization they come from. A choice of masses has often been thought of as a purely computational task, and they have to be small enough to make negligible the oscillating

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energy flow between the 'electronic' and nuclear degrees of freedom. Furthermore, in the context of Car–Parrinello Newton-type dynamics, the forces acting upon the nuclei appear to be no longer of the traditional Hellmann–Feynman type, but are corrected by the so-called Pulay term [7]. This results in the fact that nuclei do not move on the usual Born–Oppenheimer energy potential hypersurface. The source of the correction term arises from identifying the position vectors of the real nuclei with the centres of the basis set orbitals treated as parameters (see, e.g., the remarks by Pastore and co-workers [7]). These, and other problems which the Car–Parrinello Lagrangian faces, are under discussion in the literature [1–4, 6, 7].

In the present paper we aim to rigorously construct a classical mechanics Lagrangian of the 'electronic' parameter-type degrees of freedom, on the grounds of the quantum variational principle. Specifically, the construction procedure is based on a general formulation [8] (for recent publications see [9, 10]) with a certain modification of the Dirac–Frenkel time-dependent variational principle (see Dirac, Frenkel, and Langhoff and co-workers [11]). We consider a fixed trial quantity Θ depending on the family of parameters $\Xi = \alpha, \beta, \gamma, \ldots$. To minimize $E[\Theta]$ is equivalent to seeking the optimized trajectory in the domain $\mathcal{D}_\Xi$ of the given family of parameters being equipped with a *fictitious time* t dependence. This trajectory turns out to be the extremum of the appropriately derived Lagrangian of the classical system whose degrees of freedom are assigned with Θ.

The paper is organized in the following way. Section 2 focuses on the construction procedure of a classical Lagrangian and the corresponding equations of motion in the general case of choosing 'electronic' parameters. In particular it is emphasized that, in general, an 'electronic' dynamics appears to be non-Newtonian. This section ends by discussing the distinction between such 'electronic' parameters as the orbital centres on one hand, and the real nuclear positions on the other hand. The total separation of these degrees of freedom causes the forces acting upon the nuclei to coincide exactly with the Hellmann–Feynman forces, whilst the Pulay correction term begins to play the role of the force acting upon a centre-of-orbital degree of freedom. In section 3 the general algorithm is illustrated by choosing Θ to be equal to the closed-shell Hartree–Fock wavefunction. The configuration interaction wavefunction is treated in the background of the Hartree–Fock classical dynamics. This allows us to obtain explicit expressions for the masses of 'electronic' degrees of freedom in the limit of small velocities. All terms appearing in the equations of motion are derived analytically. A comparison with the Car–Parrinello Lagrangian is made. Section 5 concludes the paper with a discussion. Atomic units are used throughout the paper.

2. General molecular dynamics formalism

Consider a quantum N-electron system governed by the N-electron Hamiltonian

$$H = -\frac{1}{2}\sum_{i=1}^{N}\nabla_{r_i}^2 + \sum_{\alpha=1}^{\mathcal{M}}\frac{P_\alpha^2}{2M_\alpha} + U_{ee} + U_{en} + U_{nn} \tag{1}$$

where $U_{ee} = \sum_{1=i<j}^{N}|r_i - r_j|^{-1}$; $U_{en} = -\sum_{i=1}^{N}\sum_{\alpha=1}^{\mathcal{M}} Z_\alpha|r_i - R_\alpha|^{-1}$ and $U_{nn} = +\sum_{1=\alpha<\beta}^{\mathcal{M}} Z_\alpha Z_\beta|R_\alpha - R_\beta|^{-1}$. In (1) the vector r_i defines the position of the ith electron ($i = 1, \ldots, N$), while the αth nucleus is characterized by mass M_α, nuclear charge Z_α, position vector R_α ($\alpha = 1, \ldots, \mathcal{M}$), and the conjugated momentum P_α. Introduce

$\boldsymbol{x}_i \equiv (\boldsymbol{r}_i, s_i)$, where s_i is the zth spin projection of the ith electron, and $\boldsymbol{X}_\alpha \equiv (\boldsymbol{R}_\alpha, S_\alpha)$, for S_α being the zth spin projection of the αth nucleus. For the sake of convenience, a trial quantity Θ is identified with Ψ.

Quantum many-body theory has to deal with the fact that any exact bound-energy eigenstate of the Hamiltonian H is unknown and seems to be inaccessible. However, with an approximate trial wavefunction $\Psi(\{\boldsymbol{x}_i\}_{i=1}^N; \{\boldsymbol{X}_\alpha\}_{\alpha=1}^M)$ which by definition contains some well chosen parameters $\{\xi_i\}$, one can come close to the exact ground state by minimizing the expectation value of the energy

$$\boldsymbol{E}[\Psi] = \langle\Psi(\{\boldsymbol{x}_i\}_{i=1}^N; \{\boldsymbol{X}_\alpha\}_{\alpha=1}^M)|H|\Psi(\{\boldsymbol{x}_i\}_{i=1}^N; \{\boldsymbol{X}_\alpha\}_{\alpha=1}^M)\rangle \equiv \boldsymbol{E}_\Psi[\Xi] \tag{2}$$

with respect to the parameters set $\Xi \equiv \{\xi_i\}$, instead of the Hilbert space $\mathcal{H}$ of such Ψ for which the energy functional $\boldsymbol{E}[\Psi]$ is well defined. That results in the parametrically optimized wavefunction $\Psi_{\text{opt}} \equiv \Psi(\{\boldsymbol{x}_i\}_{i=1}^N; \{\boldsymbol{X}_\alpha\}_{\alpha=1}^M; \{\xi_k^{\text{opt}}\})$.

The procedure of minimizing $\boldsymbol{E}_\Psi[\{\xi_i\}]$ can be treated in a different way. One can assume that a certain topologically closed domain $\mathcal{D}_{\xi_i}$ exists for each set of parameters $\{\xi_i\}$ which are associated with the given and fixed trial Ψ. The minimization search starts with the initially chosen value $\boldsymbol{E}_\Psi[\{\xi_j^i\}]$ and ends at $\boldsymbol{E}_\Psi[\{\xi_j^f \equiv \xi_j^{\text{opt}}\}]$ where each $\xi_j^{i,f} \in \mathcal{D}_{\xi_j}$. Imagine a bundle of differentiable trajectories $\{\xi_i(t)\}$ linking the boundary points $\{\xi_j^i\}$ at $t = -T/2$ and $\{\xi_j^f\}$ at $t = +T/2$, and think of them as possible paths of motion in a fictitious time t of some classical system whose degrees of freedom are associated with $\{\xi_i\}$. The arc length of these trajectories can be taken as t. In terms of quantum mechanics, this fictitious system moves in the definitive domain $\mathcal{B}$ of the Hilbert space $\mathcal{H}$ consisting of unit wavefunctions $\{\Psi(\{\mathcal{R}_\kappa(t)\}; \{\zeta_j(t)\})\}_{t=-T/2}^{t=+T/2}$. Clearly, $\mathcal{B}_\Psi$ is fully determined by the form of the chosen total trial wavefunction Ψ. In other words, a trial Ψ controls the fictitious dynamics. Its extremal path optimizes the minimization search. Such a picture is useful in formally deriving a classical mechanics Lagrangian [8] on the basis of the modified Frenkel–Dirac time-dependent variational principle [11] (see [9, 10] for recent publications on this topic).

The Hamiltonian H is written in terms of real quantum mechanical variables, namely the couples of the canonical momentum and position variables of the pertinent electrons as well as in terms of the appropriate canonical conjugate variables of the nuclei. Assume that the latter ones are treated classically within the usual Born–Oppenheimer approximation. Define the Hamiltonian action

$$\mathcal{S}_{\Psi,\bar{\Psi}} \equiv \int_{-T/2}^{+T/2} \mathrm{d}t \left(\mathcal{L}^{\text{BO}}_{\Psi,\bar{\Psi}}(t) + \sum_{\alpha=1}^{M} \boldsymbol{P}_\alpha^2/2M_\alpha - U_{\text{nn}} \right) \tag{3}$$

where

$$\mathcal{L}^{\text{BO}}_{\Psi,\bar{\Psi}}(t) \equiv \langle\Psi(\{\bar{\xi}_i\})|\imath\partial/\partial t - H_{\text{BO}}(\{\boldsymbol{R}_\alpha\}_\alpha)|\Psi(\{\xi_i\})\rangle. \tag{4}$$

Here H_{BO} is the traditional Born–Oppenheimer Hamiltonian

$$H_{\text{BO}}(\{\boldsymbol{R}_\alpha\}_\alpha) = -\frac{1}{2}\sum_{i=1}^{N} \nabla_{\boldsymbol{r}_i}^2 + \sum_{1=i<j}^{N} |\boldsymbol{r}_i - \boldsymbol{r}_j|^{-1} - \sum_{i=1}^{N}\sum_{\alpha=1}^{M} Z_\alpha |\boldsymbol{r}_i - \boldsymbol{R}_\alpha|^{-1}. \tag{5}$$

Notice that the vectors defining the nuclear positions, $\{\boldsymbol{R}_\alpha\}_{\alpha=1}^M$, still appear in H_{BO}. In (4), the set Ξ of parameters is rotated to complex values where the imaginary parts of parameters

are related to momenta (see [8, 10]). This set is 'electronic' in nature and thus may include vectors $\mathcal{R}_\kappa (\kappa = 1, \ldots, \tilde{\mathcal{M}})$, the centres of the chosen spin–orbital basis set in which a trial wavefunction Ψ is always expanded:

$$\Psi(\{x_i\}_{i=1}^N) = \sum_{J=\{j_1, j_2, \ldots, j_N\}} G_J D_J(\{x_i\}_{i=1}^N) \tag{6}$$

where G_J is a linear coefficient associated with a single Slater determinant (the brackets [ ] display a determinant)

$$D_J(\{x_i\}_{i=1}^N) = (N!)^{-1/2}[\psi_{j_1}(x_1)\psi_{j_2}(x_2)\ldots\psi_{j_N}(x_N)] \tag{7}$$

in which each $\psi_i(x), i = 1, \ldots, K$ is expanded in terms of the given atomic basis spin–orbitals $\{\phi_\mu(x)\}_{\mu=1}^L$

$$\psi_i(x) = \sum_{\mu=1}^{L} c_{i\mu}\phi_\mu(x). \tag{8}$$

Here $c_{i\mu}$ is the element of the LCAO $K \times L$ matrix $\mathbf{C} \equiv (c_{i\mu})$ in the ith row and μth column, where L is the dimension of the basis set. It is worth noticing that, strictly speaking, there exists a fundamental difference between the vectors, $\{\boldsymbol{R}_\alpha\}_{\alpha=1}^{\mathcal{M}}$ and $\{\mathcal{R}_\kappa\}_{\kappa=1}^{\tilde{\mathcal{M}}}$. The former are included in H_{BO} and will become the real quantum mechanical variables if one goes beyond the usual Born–Oppenheimer approximation. The latter are just suitable parameters assigned to a trial many-electron wavefunction.

The fictitious time derivative in (4) is applied to the 'electronic' degrees of freedom. Hence, following the line of the general approach [8] (see also [9, 10]), one derives the Lagrangian of the 'electronic' classical subsystem

$$\mathcal{L}^{\mathrm{BO}}_{\Psi,\tilde{\Psi}}(t) = \frac{\imath}{2}\sum_i \left(\bar{Z}_i^{(\Xi)}\dot{\bar{\xi}}_i - Z_i^{(\Xi)}\dot{\xi}_i\right) - \tilde{E}^{\mathrm{BO}}_{\Psi,\tilde{\Psi}} \tag{9}$$

where the dot means a time derivative, $\Xi \equiv \{\xi_i\}$ and its complex conjugate $\bar{\Xi} \equiv \{\bar{\xi}_i \equiv \bar{\xi}_i\}$, where $\tilde{E}^{\mathrm{BO}}_{\Psi,\tilde{\Psi}} \equiv \langle\Psi(\bar{\Xi})|H_{\mathrm{BO}}|\Psi(\Xi)\rangle$, and where

$$Z_i^{(\Xi)} \equiv \langle\Psi(\bar{\Xi})|\partial_{\xi_i}\Psi(\Xi)\rangle \qquad \bar{Z}_i^{(\Xi)} \equiv \langle\partial_{\bar{\xi}_i}\Psi(\bar{\Xi})|\Psi(\Xi)\rangle \tag{10}$$

with $\partial_\lambda \equiv \partial/\partial\lambda$ and $\partial_{\bar{\lambda}} \equiv \partial/\partial\bar{\lambda}$.

The equations of the coupled motion of the 'electronic' and nuclear degrees of freedom are

$$\begin{pmatrix} \eta^{(\Xi\Xi)} & 0 \\ 0 & -\bar{\eta}^{(\Xi\Xi)} \end{pmatrix}\begin{pmatrix} \dot{\Xi} \\ \dot{\bar{\Xi}} \end{pmatrix} = \begin{pmatrix} \partial_{\bar{\Xi}}(\tilde{E}_{\Psi,\tilde{\Psi}} - \epsilon\Omega) \\ \partial_{\Xi}(\tilde{E}_{\Psi,\tilde{\Psi}} - \epsilon\Omega) \end{pmatrix}$$
$$\dot{R}_\alpha = P_\alpha/M_\alpha \qquad \dot{P}_\alpha = F^\alpha(\Xi, \bar{\Xi}) \tag{11}$$

where $\eta^{(\Xi\Xi)}$ is the matrix with the elements $\eta_{ij} = \imath\mathbf{T}_{ij}\mathbf{D}(\bar{\Xi}; \Xi)$ with $\mathbf{D}(\bar{\Xi}; \Xi) = \langle\Psi(\bar{\Xi})|\Psi(\Xi)\rangle$. Here $\mathbf{T}$ is the matrix differential operator with $\mathbf{T}_{ij} \equiv \partial^2_{\bar{\xi}_i\xi_j}$; Ω expresses

some possible 'electronic' constraints, and ϵ is the corresponding Lagrange multiplier. In the last line of (11)

$$F_{\mathrm{HF}}^{\alpha}(\Xi,\bar{\Xi}) \equiv -\partial_{R_\alpha}\left\{\bar{E}^{\mathrm{BO}}_{\Psi,\bar{\Psi}} + \sum_{1=\alpha<\beta}^{\mathcal{M}} Z_\alpha Z_\beta |R_\alpha - R_\beta|^{-1}\right\}$$

$$= Z_\alpha \int \mathrm{d}^3 r\, \rho_\psi(\Xi,\bar{\Xi};r)\frac{r-R_\alpha}{|r-R_\alpha|^3} + \sum_{\nu=1,\nu\neq\alpha}^{\mathcal{M}} Z_\nu Z_\alpha \frac{R_\alpha - R_\nu}{|R_\alpha - R_\nu|^3} \qquad (12)$$

is the force acting upon the αth nucleus from the remaining classical system with the 'electronic' degrees of freedom.

To conclude this section, it is worthwhile to note the following.

First, studying the evolution of the 'electronic' degrees of freedom, we introduce the fictitious time $t = t_{\mathrm{elec}}$ (as the arc length, for instance). The nuclear degrees of freedom evolve in real time, say t_{nucl}. The nuclear dynamics is physically meaningful. Since the initial 'electronic' parameters, or the initial moment of their evolution, can be chosen rather arbitrarily, one can put $t_{\mathrm{elec}} = t_{\mathrm{nucl}}$. In other words, both sorts of degrees of freedom start and end their time evolution simultaneously.

Second, generally speaking, the dynamics of the 'electronic' degrees of freedom is Lagrangian, as can be seen from (12), or non-Newtonian, i.e. the 'electronic' masses are no longer simple proportional coefficients between momenta and velocities. They determine the inertial tensor which includes the dependence on the other degrees as well as on their momenta.

Third, the motion of the 'electronic' and nuclear variables are coupled. In particular, the force F_{HF}^{α} depends on the 'lighter' variables and takes the familiar Hellmann–Feynman form because, within the present approach, the 'nuclear' variables appearing as the 'electronic' parameters (see (6) and (8)) are considered separately from the real nuclear variables. The dynamics of the former ones is generally non-Newtonian, in contrast to that of the latter ones.

3. Classical dynamics on the Hartree–Fock state

3.1. 'Electronic' equations of motion

Choose a trial Ψ in the simplest form (7) of the closed-shell Slater determinant ($N = 2M$):

$$\Psi_{\mathrm{HF}}(x_1, x_2, \ldots, x_N) = (N!)^{-1/2}\left[\psi_1(r_1)\alpha(s_1)\psi_1(r_2)\beta(s_2)\ldots\psi_M(r_N)\beta(s_N)\right]. \qquad (13)$$

Each orbital $\psi_i(r)$ is represented by (8) with the appropriate replacing of x by r. Therefore, in this particular case of the closed-shell Hartree–Fock approximation, one deals with the following 'electronic' degrees of freedom determining the fictitious classical subsystem. (i) $\mathcal{R}$ is the column vector consisting of $\mathcal{R}_\kappa, \kappa = 1, \ldots, \bar{\mathcal{M}}$, the centres of the basis set orbitals. (ii) The matrix $\mathbf{C} \equiv (c_{i\mu})$ of LCAO coefficients defined by (8). Other parameters which may appear in the expression of a basis set orbitals can be trivially included in the treatment. In the most general case of a CI-type N-electron wavefunction $\Psi(\{x_i\}_{i=1}^{N})$, the expansion coefficients G_J defined by (6), join the set of 'electronic' degrees of freedom outlined above.

LCAO parameters impose the following constraint on the dynamics of the fictitious 'electronic' subsystem:

$$\Omega_{ij} \equiv \sum_{\mu,\nu=1}^{L} \bar{c}_{i\mu} S_{\mu\nu}(\mathcal{R}_\kappa) c_{j\nu} - \delta_{ij} = 0. \tag{14}$$

In principle, the aforementioned constraints can be removed by the reparametrization (see, for instance, [12]). The CI dynamics requires an extra constraint, $\Lambda \equiv \sum_I \bar{G}_I G_I - 1 = 0$.

The Hartree–Fock Lagrangian takes the form of (9):

$$\mathcal{L}^{\mathrm{BO}}_{\mathrm{HF}}(\{\boldsymbol{R}_\alpha\}_\alpha) = \frac{\imath}{2}\left\{\sum_{\kappa=1}^{\bar{\mathcal{M}}}[\bar{Z}^{(\mathcal{R})}_\kappa \dot{\bar{\mathcal{R}}}_\kappa - Z^{(\mathcal{R})}_\kappa \dot{\mathcal{R}}_\kappa] + \sum_{i=1}^{K}\sum_{\nu=1}^{L}[\bar{Z}^{(\mathbf{C})}_{i\nu}\dot{\bar{c}}_{i\nu} - Z^{(\mathbf{C})}_{i\nu}\dot{c}_{i\nu}]\right\}$$
$$- \tilde{E}_{\mathrm{HF}}[\bar{\mathcal{R}}, \bar{\mathbf{C}}; \mathcal{R}, \mathbf{C}]. \tag{15}$$

The next step is to derive the equations of motion of the 'electronic' degrees of freedom:

$$\begin{pmatrix} \eta^{(\mathcal{R}\mathcal{R})} & \eta^{(\mathcal{R}\mathbf{C})} & 0 & 0 \\ \eta^{(\mathbf{C}\mathcal{R})} & \eta^{(\mathbf{C}\mathbf{C})} & 0 & 0 \\ 0 & 0 & -\bar{\eta}^{(\mathcal{R}\mathcal{R})} & -\bar{\eta}^{(\mathcal{R}\mathbf{C})} \\ 0 & 0 & -\bar{\eta}^{(\mathbf{C}\mathcal{R})} & -\bar{\eta}^{(\mathbf{C}\mathbf{C})} \end{pmatrix} \begin{pmatrix} \dot{\mathcal{R}} \\ \dot{\mathbf{C}} \\ \dot{\bar{\mathcal{R}}} \\ \dot{\bar{\mathbf{C}}} \end{pmatrix} \equiv \begin{pmatrix} \partial_{\bar{\mathcal{R}}} & (\tilde{E}_{\mathrm{HF}} - \sum_{ij}\epsilon_{ij}\Omega_{ij}) \\ \partial_{\bar{\mathbf{C}}} & (\tilde{E}_{\mathrm{HF}} - \sum_{ij}\epsilon_{ij}\Omega_{ij}) \\ \partial_{\mathcal{R}} & (\tilde{E}_{\mathrm{HF}} - \sum_{ij}\epsilon_{ij}\Omega_{ij}) \\ \partial_{\mathbf{C}} & (\tilde{E}_{\mathrm{HF}} - \sum_{ij}\epsilon_{ij}\Omega_{ij}) \end{pmatrix}. \tag{16}$$

The symbolic column in the RHS of (16) is the generalized force matrix. Each element of this matrix is composed of two terms. The first is the contribution of the proper force and the second is the so-called contribution of the 'constraint'. The former is expressed as follows. For the $\mathcal{R}$th force:

$$\partial_{\mathcal{R}_\alpha} E_{\mathrm{HF}} = \langle \Psi_{\mathrm{HF}}(\bar{\mathcal{R}}; \bar{\mathbf{C}}) | H_{\mathrm{BO}} | \partial_{\mathcal{R}_\alpha} \Psi_{\mathrm{HF}}(\mathcal{R}; \mathbf{C}) \rangle \qquad \alpha = 1, \ldots, \bar{\mathcal{M}}$$

and for the $\mathbf{C}$th force:

$$\partial_{c_{i\mu}} E_{\mathrm{HF}} = 4 \sum_{\nu} F_{\mu\nu} \bar{c}_{i\nu} \qquad i = 1, \ldots, K \quad \mu = 1, \ldots, L. \tag{17}$$

Here we have used the formula for the derivative of the Hartree–Fock energy with respect to LCAO coefficients (see, e.g., [13]); $F_{\mu\nu}$ is the (μ, ν) element of the Fock matrix.

The elements of the matrix η are:

$$\eta^{(\mathcal{R}\mathcal{R})}_{\kappa\lambda} = \imath \langle \partial_{\bar{\mathcal{R}}_\kappa} \Psi_{\mathrm{HF}}(\bar{\mathcal{R}}; \bar{\mathbf{C}}) | \partial_{\mathcal{R}_\lambda} \Psi_{\mathrm{HF}}(\mathcal{R}; \mathbf{C}) \rangle$$

$$\eta^{(\mathbf{C}\mathcal{R})}_{i\mu\kappa} = 2\imath \frac{\partial}{\partial \mathcal{R}_\kappa} \{ [\langle \psi_1 | \psi_1 \rangle \ldots \langle \psi_{i-1} | \psi_{i-1} \rangle \langle \phi_\mu | \psi_i \rangle \langle \psi_{i+1} | \psi_{i+1} \rangle \ldots \langle \psi_M | \psi_M \rangle]$$
$$\times [\langle \psi_1 | \psi_1 \rangle \ldots \langle \psi_{i-1} | \psi_{i-1} \rangle \langle \psi_i | \psi_i \rangle \langle \psi_{i+1} | \psi_{i+1} \rangle \ldots \langle \psi_M | \psi_M \rangle] \}$$

$$\eta^{(\mathbf{C}\mathbf{C})}_{i\mu,j\nu} = 2\imath \begin{cases} 2\sum_{\delta} c_{i\delta} S_{\mu\delta} \sum_{\zeta} \bar{c}_{j\zeta} S_{\zeta\nu} - \sum_{\kappa} c_{j\kappa} S_{\mu\kappa} \sum_{\delta} \bar{c}_{i\delta} S_{\delta\nu} & i\mu \neq j\nu \\ S_{\mu\nu} + \sum_{\delta} c_{i\delta} S_{\mu\delta} \sum_{\zeta} \bar{c}_{i\zeta} S_{\zeta\nu} & \text{otherwise.} \end{cases} \tag{18}$$

Evaluation of the $\mathcal{R}\mathcal{R}$th matrix elements and the $\mathcal{R}$th forces is fully determined by the functional form of the chosen orbital basis set $\{\phi_\mu(\boldsymbol{r})\}_{\mu=1}^{L}$. If they are chosen as contracted Gaussians, for instance, the aforementioned matrix elements can be given in the closed analytical form via the familiar connection formulae (see, e.g., [14]).

3.2. Inertia tensor

Consider (16): partition the 'electronic' variables, $\mathcal{R}$ and $\mathbf{C}$, into their real and imaginary parts (see [8, 9] also):

$$\begin{aligned} \mathcal{R}_\kappa &= \frac{1}{\sqrt{2}}(\alpha_\kappa + \imath\beta_\kappa) \qquad \kappa = 1, \ldots \tilde{\mathcal{M}} \\ c_{i\mu} &= \frac{1}{\sqrt{2}}(\gamma_{i\mu} + \imath\delta_{i\mu}) \qquad i = 1, \ldots, K \quad \mu = 1, \ldots, L. \end{aligned} \tag{19}$$

Rewrite (16) in terms of the new variables:

$$2\begin{pmatrix} \mathbf{U}^{(\mathcal{RR})} & \mathbf{U}^{(\mathcal{RC})} & \mathbf{V}^{(\mathcal{RR})} & \mathbf{V}^{(\mathcal{RC})} \\ \mathbf{U}^{(\mathcal{RC})} & \mathbf{U}^{(\mathbf{CC})} & -\mathbf{V}^{(\mathcal{RC})} & \mathbf{V}^{(\mathbf{CC})} \\ -\mathbf{V}^{(\mathcal{RR})} & \mathbf{V}^{(\mathcal{RC})} & \mathbf{U}^{(\mathcal{RR})} & \mathbf{U}^{(\mathcal{RC})} \\ \mathbf{V}^{(\mathcal{RC})} & -\mathbf{V}^{(\mathbf{CC})} & \mathbf{U}^{(\mathcal{RC})} & \mathbf{U}^{(\mathbf{CC})} \end{pmatrix} \begin{pmatrix} \dot{\alpha} \\ \dot{\gamma} \\ \dot{\eta} \\ \dot{\delta} \end{pmatrix} \equiv \begin{pmatrix} \partial_\eta \\ \partial_\delta \\ -\partial_\alpha \\ -\partial_\gamma \end{pmatrix} \tilde{E}_{\mathrm{HF}} \tag{20}$$

where $\alpha = (\alpha_\kappa)$, $\eta = (\beta_\kappa)$, $\gamma = (\gamma_{i\mu})$ and $\delta = (\delta_{i\mu})$. In (20) the block matrices are defined as follows:

$$\begin{aligned} \mathbf{U}^{(\mathcal{RR})}_{\kappa\zeta} &= \left(\frac{\partial^2}{\partial\alpha_\kappa\partial\alpha_\zeta} + \frac{\partial^2}{\partial\beta_\kappa\partial\beta_\zeta}\right)\mathbf{D}(\alpha;\gamma;\eta;\delta) \\ \mathbf{U}^{(\mathcal{RC})}_{\kappa i\mu} &= \left(\frac{\partial^2}{\partial\alpha_\kappa\partial\gamma_{i\mu}} + \frac{\partial^2}{\partial\beta_\kappa\partial\delta_{i\mu}}\right)\mathbf{D}(\alpha;\gamma;\eta;\delta) \\ \mathbf{U}^{(\mathbf{CC})}_{i\mu j\nu} &= \left(\frac{\partial^2}{\partial\gamma_{i\mu}\partial\gamma_{j\nu}} + \frac{\partial^2}{\partial\delta_{i\mu}\partial\delta_{j\nu}}\right)\mathbf{D}(\alpha;\gamma;\eta;\delta) \\ \mathbf{V}^{(\mathcal{RR})}_{\kappa\zeta} &= \left(\frac{\partial^2}{\partial\alpha_\kappa\partial\beta_\zeta} - \frac{\partial^2}{\partial\beta_\kappa\partial\alpha_\zeta}\right)\mathbf{D}(\alpha;\gamma;\eta;\delta) \\ \mathbf{V}^{(\mathcal{RC})}_{\kappa i\mu} &= \left(\frac{\partial^2}{\partial\alpha_\kappa\partial\delta_{i\mu}} - \frac{\partial^2}{\partial\beta_\kappa\partial\gamma_{i\mu}}\right)\mathbf{D}(\alpha;\gamma;\eta;\delta) \\ \mathbf{V}^{(\mathbf{CC})}_{i\mu j\nu} &= \left(\frac{\partial^2}{\partial\gamma_{i\mu}\partial\delta_{j\nu}} - \frac{\partial^2}{\partial\delta_{i\mu}\partial\gamma_{j\nu}}\right)\mathbf{D}(\alpha;\gamma;\eta;\delta). \end{aligned} \tag{21}$$

The matrices $\mathbf{V}^{(\mathcal{RR})}$ and $\mathbf{V}^{(\mathbf{CC})}$ are asymmetric. Hence, in particular, their diagonal elements vanish.

Assume now that each $\mathcal{R}_\kappa$ and each $c_{i\mu}$ are very close to the real values, $\alpha_\kappa \gg \beta_\kappa$; $\gamma_{i\mu} \gg \delta_{i\mu}$, so that Ψ_{HF} of the form (13) with complex parameters becomes close to the real one. Assume further that the non-diagonal elements of the matrices $\mathbf{U}^{(\mathcal{RR})}$ and $\mathbf{U}^{(\mathbf{CC})}$ are negligibly small with respect to their diagonal elements. Let us also assume that these diagonal elements give the dominant contribution to the equations of motion (20). To this order of approximation, we now make a comparison of (16) with the canonical Hamiltonian equations of motion. It results in the following explicit form for the coordinate and conjugate momentum variables:

$$\begin{aligned} Q_\kappa &= \alpha_\kappa/\sqrt{2} = \mathrm{Re}\,\mathcal{R}_\kappa \\ P_\kappa &= \sqrt{2}\langle\partial\Psi_{\mathrm{HF}}(\alpha;\gamma)/\partial\alpha_\kappa|\partial\Psi_{\mathrm{HF}}(\alpha;\gamma)/\partial\alpha_\kappa\rangle\beta_\kappa = 2\mathcal{K}_\kappa\mathrm{Im}\,\mathcal{R}_\kappa \\ q_{i\mu} &= \gamma_{i\mu}/\sqrt{2} = \mathrm{Re}\,c_{i\mu} \\ p_{i\mu} &= \sqrt{2}\langle\partial\Psi_{\mathrm{HF}}(\alpha;\gamma)/\partial c_{i\mu}|\partial\Psi_{\mathrm{HF}}(\alpha;\gamma)/\partial c_{i\mu}\rangle\delta_{i\mu} = 2\mathcal{K}_{i\mu}\mathrm{Im}\,c_{i\mu}. \end{aligned} \tag{22}$$

Expand the 'electronic' Hamiltonian function $\tilde{E}_{\mathrm{HF}}$ in terms of $\alpha_\kappa, \kappa = 1, \ldots, \tilde{\mathcal{M}}$ and $\gamma_{i\mu}, i = 1, \ldots, K; \mu = 1, \ldots, L$ to this order of accuracy and compare the obtained formula with the familiar bilinear form of the kinetic energy. One finds the formula for the mass $m_i(\mathrm{Re}\ \Xi)$ of the variable ξ_i, the corresponding diagonal elements of the inertia tensor (see also Kermin and Koonin [8]):

$$\begin{aligned} m_\kappa^{-1}(\alpha;\gamma) &= (2\mathcal{K}_\kappa)^{-2}\{2\langle\partial\Psi_{\mathrm{HF}}(\alpha;\gamma)/\partial\alpha_\kappa|H_{\mathrm{BO}}|\partial\Psi_{\mathrm{HF}}(\alpha;\gamma)/\partial\alpha_\kappa\rangle \\ &\quad - \langle\Psi_{\mathrm{HF}}(\alpha;\gamma)|H_{\mathrm{BO}}|\partial^2\Psi_{\mathrm{HF}}(\alpha;\gamma)/\partial{\alpha_\kappa}^2\rangle \\ &\quad - \langle\partial^2\Psi_{\mathrm{HF}}(\alpha;\gamma)/\partial{\alpha_\kappa}^2|H_{\mathrm{BO}}|\Psi_{\mathrm{HF}}(\alpha;\gamma)\rangle\} \\ m_{i\mu}^{-1}(\alpha;\gamma) &= (2\mathcal{K}_{i\mu})^{-2}\{2\langle\partial\Psi_{\mathrm{HF}}(\alpha;\gamma)/\partial c_{i\mu}|H_{\mathrm{BO}}|\partial\Psi_{\mathrm{HF}}(\alpha;\gamma)/\partial c_{i\mu}\rangle \\ &\quad - \langle\Psi_{\mathrm{HF}}(\alpha;\gamma)|H_{\mathrm{BO}}|\partial^2\Psi_{\mathrm{HF}}(\alpha;\gamma)/\partial{c_{i\mu}}^2\rangle \\ &\quad - \langle\partial^2\Psi_{\mathrm{HF}}(\alpha;\gamma)/\partial{c_{i\mu}}^2|H_{\mathrm{BO}}|\Psi_{\mathrm{HF}}(\alpha;\gamma)\rangle\}. \end{aligned} \tag{23}$$

It follows immediately from the last expression in (23) that, to the mentioned order of accuracy, the LCAO coefficient's mass $m_{i\mu}$ becomes equal to $1/2F_{\mu\mu}$, the μth diagonal element of the Fock matrix. The latter in turn depends also upon all the variables under study: LCAO coefficients accompanying two-electron integrals, $\{\mathcal{R}_\kappa\}$ involved in one- and two-electron integrals and the overlap matrix, and finally, $\{\boldsymbol{R}_\alpha\}$ appearing in the one-electron integrals of the electron–nuclear 'external' potential. According to (17), the frequency of small oscillations of the $c_{i\mu}$th degree of freedom about the global minimum is determined by $2F_{\mu\mu}$. Hence, in summary, the masses of the LCAO coefficients are different for the different AO orbitals. One sees also from (23) that the corresponding masses of the $\mathcal{R}_\kappa$th degrees of freedom are no longer constant and are not equal to the appropriate nuclear masses, at least for small velocities in all degrees of freedom in question. To evaluate these masses by means of the first formula in (23), one should specify an orbital basis set. In the case of the dynamics on the configuration interaction quantum state, the 'electronic' inertia tensor becomes more complicated owing to the contribution of the additional degrees of freedom related with CI expansion coefficients. In particular, extending the assumption of small enough velocities to the CI degrees of freedom and neglecting the non-diagonal elements of the corresponding matrices in the appropriate equations of motion, one obtains that $m_{G_l}^{-1} = E^{\mathrm{BO}}[D_l]$, the expectation value of H_{BO} in the state described by the Slater determinant D_l. Therefore, one can conclude that the equations of motion of the 'electronic' degrees of freedom derived above are of non-Newtonian type.

3.3. Dissipation

Assume the validity of the bilinear form of the 'electronic' kinetic energy. This assumption is, in particular, justified in the aforementioned case of small enough velocities. The total Hartree–Fock Hamiltonian function of the 'electronic' and nuclear subsystems then takes the expression

$$\tilde{E}_{\mathrm{HF}}[\{\xi_i, p_i\}; \{\boldsymbol{R}_\alpha, \boldsymbol{P}_\alpha\}] = \frac{1}{2}\sum_{ij} m_{ij}^{-1} p_i p_j + \sum_{\alpha=1}^{\mathcal{M}} + U_{\mathrm{nn}} + U_{\mathrm{ee}}^{\mathrm{HF}} + U_{\mathrm{en}}^{\mathrm{HF}} \tag{24}$$

where

$$U_{\mathrm{ee}}^{\mathrm{HF}} = \langle\Psi_{\mathrm{HF}}(\{\xi_i\})|U_{\mathrm{ee}}|\Psi_{\mathrm{HF}}(\{\xi_i\})\rangle \qquad U_{\mathrm{en}}^{\mathrm{HF}} = \langle\Psi_{\mathrm{HF}}(\{\xi_i\})|U_{\mathrm{en}}|\Psi_{\mathrm{HF}}(\{\xi_i\})\rangle. \tag{25}$$

The set $\{\xi_i\}$ of the electronic parameters in question is comprised of LCAO coefficients, $\{c_{i\mu}\}$, and of the centres $\{\mathcal{R}_\kappa\}$ of the basis AO. Choose, for instance, $\{c_{i\mu} = c_{i\mu}^{(o)}\}$ (not too far away from the equilibrium point $\{c_{i\mu}^f\}$) in the subdomain of parameters where the form (24) is well defined. The values of the remaining parameters, $\{\mathcal{R}_\kappa\}$ and $\{\boldsymbol{R}_\alpha\}$, yield the local minimum conditions

$$\left[\partial_{\mathcal{R}_\kappa}(U_{ee}^{HF} + U_{en}^{HF}\right]_{(o)} = 0 \qquad \left[\partial_{\boldsymbol{R}_\alpha}(U_{nn} + U_{en}^{HF}\right]_{(o)} = 0 \tag{26}$$

where the subscript (o) is shorthand for $\left(\{c_{i\mu}^{(o)}\}; \{\mathcal{R}_\kappa^{(o)}\}; \{\boldsymbol{R}_\alpha^{(o)}\}\right)$. It is worth noting that the local minimum conditions for centres of the basis set orbitals are separated from those for the nuclear positions. Expanding the Hamiltonian function (24) in the neighbourhood of the point (o) in the domain of the electronic parameters and 3D vectors of the nuclear positions, one obtains

$$\begin{aligned}
\tilde{E}_{HF}[\{\xi_i, p_i\}; \{\boldsymbol{R}_\alpha, \boldsymbol{P}_\alpha\}] &= U_{nn,(o)} + U_{ee,(o)}^{HF} + U_{en,(o)}^{HF} \\
&+ \frac{1}{2}\sum_{ij} m_{ij,(o)}^{-1}\left\{1 - m_{ij,(o)}^{-1}\left[\sum_l (\xi_l - \xi_l^{(o)})[\partial_{\xi_l} m_{ij}]_{(o)}\right.\right. \\
&\left.\left. + \sum_{\alpha=1}^{\mathcal{M}} (\boldsymbol{R}_\alpha - \boldsymbol{R}_\alpha^{(o)})[\partial_{\boldsymbol{R}_\alpha} m_{ij}]_{(o)}\right]\right\} p_i p_j \\
&+ \sum_{\alpha=1}^{\mathcal{M}} \boldsymbol{P}_\alpha^2/2M_\alpha + \frac{1}{2}\sum_{\alpha,\beta=1}^{\mathcal{M}} (\boldsymbol{R}_\alpha - \boldsymbol{R}_\alpha^{(o)})(\boldsymbol{R}_\beta - \boldsymbol{R}_\beta^{(o)})[\partial_{\boldsymbol{R}_\alpha \boldsymbol{R}\beta}^2 (U_{nn} + U_{en}^{HF})]_{(o)} \\
&+ \frac{1}{2}\sum_{ij} (\xi_i - \xi_i^{(o)})(\xi_j - \xi_j^{(o)})[\partial_{\xi_i \xi_j}^2](U_{ee}^{HF} + U_{en}^{HF})]_{(o)} + \frac{1}{2}\sum_i \sum_{\alpha=1}^{\mathcal{M}} (\xi_i - \xi_i^{(o)}) \\
&\times (\boldsymbol{R}_\alpha - \boldsymbol{R}_\alpha^{(o)})[\partial_{\boldsymbol{R}_\alpha \xi_i}^2 U_{en}^{HF}]_{(o)} + (\text{second-order terms})
\end{aligned} \tag{27}$$

where all the quantities equipped with the subscript (o) are evaluated at the local minimum determined above. As seen from (27), the expansion of the Hartree–Fock Hamiltonian function involves the Pulay-type gradient of the Hellmann–Feynman force.

Consider the kinetic energy part of the expansion (27). A couple of the diagonal expansion coefficients can be easily evaluated:

$$\begin{aligned}
\tfrac{1}{2} m_{i\mu i\mu}^{-2} \partial_{c_{i\mu}} m_{i\mu i\mu} &= -\sum_k c_{k\nu}[2(\mu\mu|\nu k) - (\mu\nu|k\mu)] \\
\tfrac{1}{2} m_{i\mu i\mu}^{-2} \partial_{\boldsymbol{R}_\alpha} m_{i\mu i\mu} &= -Z_\alpha \int \mathrm{d}^3 r \; |\phi_\mu(r)|^2 \frac{\boldsymbol{r} - \boldsymbol{R}_\alpha}{|\boldsymbol{r} - \boldsymbol{R}_\alpha|^3}
\end{aligned} \tag{28}$$

where $(\mu\nu|\pi\delta)$ is the two-electron repulsion integral. The last expression in (28) demonstrates that the μth orbital contribution to the electronic part of the Hellmann–Feynman force determines the curvature of the diagonal of the inertia tensor of the $c_{i\mu}$th degree of freedom. The expression for $\frac{1}{2} m_{i\mu i\mu}^{-2} \partial_{\mathcal{R}_\kappa} m_{i\mu i\mu}$ is rather cumbersome to present in explicit form. It includes the gradients of one- and two-electron integrals and the overlap matrix of the basis set with respect to $\mathcal{R}_\kappa$.

In a course of the $c_{i\mu}$th degree of freedom from the chosen value, $c_{i\mu}^{(o)}$, to the global minimum one, $c_{i\mu}^f$, the energy stored early in this degree of freedom dissipates to all other degrees of freedom, both the 'electronic' and the nuclear ones. Explicitly, the dissipation

terms appear in particular in the following equations of motion for the corresponding momenta:

$$2\dot{p}_{j\nu} = \sum_k c_{k\nu}[2(\mu\mu|\nu k) - (\mu\nu|k\mu)]\dot{q}_{i\mu}^2 + \dots$$

$$2\dot{\mathcal{P}}_\kappa = \partial_{\mathcal{R}_\kappa} m_{i\mu i\mu}\dot{q}_{i\mu}^2 + \sum_{\alpha=1}^{\mathcal{M}}(\boldsymbol{R}_\alpha - \boldsymbol{R}_\alpha^{(0)})[\partial_{\mathcal{R}_\kappa}\boldsymbol{F}_{\mathcal{HF}}^\alpha(\Xi, \Xi)]_{(0)} + \dots$$

$$2\dot{\boldsymbol{P}}_\alpha = -Z_\alpha \int \mathrm{d}^3\boldsymbol{r}|\phi_\mu(\boldsymbol{r})|^2 \frac{\boldsymbol{r} - \boldsymbol{R}_\alpha}{|\boldsymbol{r} - \boldsymbol{R}_\alpha|^3}\dot{q}_{i\mu}^2 + \sum_{\kappa=1}^{\tilde{\mathcal{M}}}(\mathcal{R}_\kappa - \mathcal{R}_\kappa^{(0)})[\partial_{\mathcal{R}_\kappa}\boldsymbol{F}_{\mathcal{HF}}^\alpha(\Xi, \Xi)]_{(0)} + \dots . \tag{29}$$

It follows from (29) that the dissipation of energy from one of the LCAO degrees of freedom is determined by the square of its velocity, with the coefficient expressed in terms of the curvature of the inertia tensor. Such dissipation is absolutely absent in the Car–Parrinello scheme.

3.4. Model example

To illustrate the formalism, consider the following one-dimensional model Hamiltonian:

$$H = -\frac{1}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{1}{2M}\frac{\mathrm{d}^2}{\mathrm{d}R^2} + U(r; R) + U(R) \equiv H_{\mathrm{BO}} + U(R) \tag{30}$$

with the potential

$$U(r; R) = 2D[\mathrm{e}^{-\beta R}\cosh(2\beta r) - 2\mathrm{e}^{-\beta R/2}\cosh(\beta r)] \tag{31}$$

chosen in the symmetric double-Morse form ($D > 0$).

On the one hand, the Hamiltonian (30) is the 1D analogue of the general one given by (1) in the particular case of H_2^+ with a double-Morse electron–nuclear interaction. On the other hand, it is widely used in studies of proton dynamics in symmetric hydrogen-bonded bridges A–H...A (see [15] and references therein). In both cases mentioned, the coordinate r refers to a lighter subsystem (an electron in the former case and a proton in the latter case) with mass m, while R is assigned to the heavier subsystem with relative mass M. The origin of the reference frame is chosen at the centre of mass of the heavier subsystem.

Choose a trial unit wavefunction of the lighter subsystem described by the Born–Oppenheimer Hamiltonian H_{BO}:

$$\Psi(r; \mathcal{R}) = \sqrt{\alpha}\exp(-\alpha|r - \mathcal{R}^2|) \qquad \mathcal{R} = \mathcal{R}_1 + \imath\mathcal{R}_2. \tag{32}$$

The corresponding Lagrangian of this subsystem takes the form

$$\mathcal{L}(R) = -4\alpha\frac{\mathrm{d}}{\mathrm{d}t}(\mathcal{R}_1\mathcal{R}_2) - E(\mathcal{R}_1, \mathcal{R}_2; R) \tag{33}$$

where the Hamiltonian function is

$$E(\mathcal{R}_1, \mathcal{R}_2; R) = 4\alpha^2 D\left(\frac{\mathrm{e}^{-\beta R}}{4(\alpha^2 - \beta^2)}\cosh[2\beta(\mathcal{R}_1^2 - \mathcal{R}_2^2)]\right.$$
$$\left. - 2\frac{\mathrm{e}^{-\beta\frac{R}{2}}}{4\alpha^2 - \beta^2}\cosh[\beta(\mathcal{R}_1^2 - \mathcal{R}_2^2)]\right). \tag{34}$$

The appropriate equations of motion follow directly from (33):

$$\begin{aligned} 8\imath\alpha^2(\mathcal{R}_1^2+\mathcal{R}_2^2)(\dot{\mathcal{R}}_1+\dot{\mathcal{R}}_2) &= (\partial_{\mathcal{R}_1}+\imath\partial_{\mathcal{R}_2})E(\mathcal{R}_1,\mathcal{R}_2;R) \\ -8\imath\alpha^2(\mathcal{R}_1^2+\mathcal{R}_2^2)(\dot{\mathcal{R}}_1-\dot{\mathcal{R}}_2) &= (\partial_{\mathcal{R}_1}-\imath\partial_{\mathcal{R}_2})E(\mathcal{R}_1,\mathcal{R}_2;R) \end{aligned} \tag{35}$$

or in a simpler form

$$\begin{aligned} 4\alpha^2(\mathcal{R}_1^2+\mathcal{R}_2^2)\dot{\mathcal{R}}_2 &= -\partial_{\mathcal{R}_1}E(\mathcal{R}_1,\mathcal{R}_2;R) \\ 4\alpha^2(\mathcal{R}_1^2+\mathcal{R}_2^2)\dot{\mathcal{R}}_1 &= \partial_{\mathcal{R}_2}E(\mathcal{R}_1,\mathcal{R}_2;R) \end{aligned} \tag{36}$$

with the initial condition $\mathcal{R}_1(0)=\mathcal{R}_0\geqslant 0$ and $\mathcal{R}_2(0)=0$. The equations of motion (36) look like canonical equations, if taking the limit of small velocities; we define the coordinate Q and its conjugate momentum P as follows:

$$Q=\mathcal{R}_1 \qquad P=4\alpha^2(\mathcal{R}_1^2+\mathcal{R}_2^2)\mathcal{R}_2. \tag{37}$$

To this order, inverting (37) results in $\mathcal{R}_2=P/4\alpha^2Q^2$.

One also finds with the help of (36) that, in the $(\mathcal{R}_1,\mathcal{R}_2)$ plane, there exists a relationship of the hyperbola type:

$$\left(\frac{\mathcal{R}_1(t)}{\mathcal{R}_0}\right)^2-\left(\frac{\mathcal{R}_2(t)}{\mathcal{R}_0}\right)^2=1 \tag{38}$$

with vertices $\pm\mathcal{R}_0$. The hyperbola (38) divides the $(\mathcal{R}_1,\mathcal{R}_2)$ plane into three regions, two of them embedded by its left and right branches, and one in between ($\mathcal{R}_0\neq 0$). The latter, so-called 'tunneling' region, is classically forbidden in our case. This pictorially resembles the display of semiclassically quantized trajectories of H_2^+ obtained by Strand and Reinhardt [16] (see also [17]).

Equation (38) determines the allowed regions of motion of the lighter subsystem. The pair of canonical variables presented in (37) is well defined in a small neighbourhood of $\mathcal{R}_1=\pm\mathcal{R}_0$, the vertices of a hyperbola (38). To extend their definition to other $\mathcal{R}_1\neq\mathcal{R}_0$, say the point $\mathcal{R}_1=\mathcal{R}_1^0>\mathcal{R}_0$ settled on the right branch, we put $\mathcal{R}_1(t)=\mathcal{R}_1^0+Q$, $\mathcal{R}_2(t)=\mathcal{R}_2^0+y$ with $\mathcal{R}_2^0=\sqrt{[\mathcal{R}_1^0]^2-[\mathcal{R}_0]^2}$. The expansion of the Hamiltonian function in powers of Q and y to second order, and the insertion of the resultant expression into the equations of motion, with a comparison with those in the canonical Hamiltonian form give us the new canonical conjugate variables at this point of the hyperbola: Q and $P=4\alpha^2[2(\mathcal{R}_1^0)^2-(\mathcal{R}_0)^2]y$. Substitute them into the Hamiltonian function instead of the original $\mathcal{R}_{1,2}$. Expand the obtained function in the powers of P, Q to second order. One gets the following:

$$\mathcal{H}(\mathcal{R}_1^0,\mathcal{R}_0;R)=\frac{1}{2m}(p+p_0)^2+\tfrac{1}{2}k(q-q_0)^2-\lambda pq+\mathcal{H}_0(\mathcal{R}_1^0,\mathcal{R}_0;R) \tag{39}$$

where we have used the following notation:

$$m^{-1}=\frac{D\beta(\sigma_1-\rho_1)}{\alpha^4\kappa}$$

$$k=32\alpha^2D\beta\left(\beta\mathcal{R}_1^0(2\rho_2-\sigma_2)+\frac{\rho_1-\sigma_1}{2}\right)$$

$$q_o = \frac{\mathcal{R}_1^o(\rho_1 - \sigma_1)}{2\beta\mathcal{R}_1^o(2\rho_2 - \sigma_2) + (\rho_1 - \sigma_1)}$$

$$\lambda = \frac{4D\beta^2\mathcal{R}_1^o\sqrt{\delta}}{\kappa}(2\rho_2 - \sigma_2)$$

$$p_o = 4\alpha^2\kappa\delta^{1/2}$$

$$\mathcal{H}_o = 4\alpha^2 D(\rho_2 - 2\sigma_2) + 8\alpha^2 D\beta\delta(\rho_1 - \sigma_1) - \frac{8\alpha^2\beta\mathcal{R}_1^{o2}(\sigma_1 - \rho_1)^2}{2\beta\mathcal{R}_1^o(2\rho_2 - \sigma_2) + (\rho_1 - \sigma_1)} \tag{40}$$

with

$$\begin{aligned}
\rho_1 &= \frac{\exp(-\beta R)\sinh 2\beta\mathcal{R}_o^2}{4(\alpha^2 - \beta^2)} \\
\rho_2 &= \frac{\exp(-\beta R)\cosh 2\beta\mathcal{R}_o^2}{4(\alpha^2 - \beta^2)} \\
\sigma_1 &= \frac{\exp(-\beta R/2)\sinh \beta\mathcal{R}_o^2}{4\alpha^2 - \beta^2} \\
\sigma_2 &= \frac{\exp(-\beta R/2)\cosh \beta\mathcal{R}_o^2}{4\alpha^2 - \beta^2}
\end{aligned} \tag{41}$$

$$\kappa = 2\mathcal{R}_1^{o2} - \mathcal{R}_o^2 \qquad \delta = \mathcal{R}_1^{o2} - \mathcal{R}_o^2.$$

Thus, as follows, all the fictitious quantities determining the Lagrangian, such as the mass, harmonic force constant, and so on, depend upon the nuclear variable R. The solution of the corresponding equations of motion is straightforward to obtain:

$$\begin{aligned}
p &= \frac{k(p_o/m - \lambda q_o)}{\omega^2}(\cos\omega t - 1) \\
q &= \frac{(p_o/m - \lambda q_o)}{\omega^2}(\lambda\cos\omega t + \omega\sin\omega t) + q_o - \frac{\lambda(p_o/m - \lambda q_o)}{\omega^2}
\end{aligned} \tag{42}$$

where the frequency $\omega^2 = (k/m) - \lambda^2$. Thus, the lighter subsystem performs finite oscillations iff first, the mass m is positive, i.e. $\sigma_1 - \rho_1 > 0$, and second the harmonic force constant k and the harmonic frequency ω^2 both become positive if the following double-side inequality holds:

$$\beta\mathcal{R}_1^o[1 - \sqrt{1 - \alpha^2\delta}] < \frac{\sigma_1 - \rho_1}{2\rho_2 - \sigma_2} < \beta\mathcal{R}_1^o[1 + \sqrt{1 - \alpha^2\delta}] \tag{43}$$

with $\alpha^2\delta < 1$. These equations are treated as the constraints imposed on the admissible α, β and R. The electronic component of the Hellmann–Feynman force depends upon the couple of conjugate variables of the lighter subsystem.

4. Concluding remarks

The procedure of constructing a fictitious classical Lagrangian on a set of degrees of freedoms playing the role of parameters in a given trial quantum quantity Θ has been elaborated. The resultant equations of motion of parameters evolving in a certain time determine the optimal trajectory. This trajectory in the parametric space being substituted from point to point into Θ yields the path in the corresponding domain of admissible Θ which can be obtained via minimizing the quantum many-electron functional $E[\Theta]$ of energy. In this sense, the above procedure reveals the rigorous accord with the quantum many-electron variational principle.

The basic concern was to develop explicitly this procedure in the common case of the usual Born–Oppenheimer approximation, with Θ being a many-electron wavefunction Ψ. The commonest parameters of Ψ are LCAO coefficients, centres of basis set orbitals, and CI expansion coefficients. All of them were involved in the aforementioned procedure to obtain the corresponding classical Lagrangian in the explicit form and the appropriate equations of motion as well.

A clear-cut borderline has been drawn to separate 'electronic' parameters, such as centres of basis set orbitals, from the radius vectors of positions of nuclei. The main reasons were the following. First, the former ones are artificial by their very nature, in comparison with the latter which are quantum operators from the beginning (in our case from (1)). Assuming semiclassicity of the latter, the dynamics of nuclei appears to be Newtonian and occurs on the Born–Oppenheimer potential energy hypersurface. On the contrary, the dynamics of those centres is in general non-Newtonian, and their inertia tensor depends functionally on all the parameters under study and also on the nuclear positions. This is the second reason. The complete ignorance of differences between centres of orbitals and positions of nuclei leads primarily to global renormalizing of the nuclear masses. That is a price to be paid. The renormalized masses organize into the appropriate tensor of inertia, depending on all 'electronic' degrees of freedom and differing in its form from one particular problem to another, say from Ψ to Φ. The resultant equations of motion lose their simple and pleasant Newtonian form. The situation appears even more complicated beyond the Born–Oppenheimer approximation, where similar 'nuclear' parametric degrees of freedom must be introduced. However, made locally, for example at the very start of the optimal trajectory, this ignorance will perhaps be useful.

Finally, we remark upon one nuance related to the elaborated procedure. It refers to the case when Θ is replaced by the one-electron density ρ. Within the density functional formulation of the self-consistent field developed in [5] (ch. 8.3e and 8.4e), the above procedure consists of two stages. In the first stage, one creates a classical Lagrangian that governs a fictitious dynamics of parameters associated with a trial ρ under the parameters of a 'host' wavefunction to be fixed (the so-called charge consistency with a 'host' wavefunction). The second stage is needed to construct a classical Lagrangian on a set of parameters of a 'host' wavefunction (the 'host' consistency). Both Lagrangians result in coupled equations of motion. Solving them, one finds the optimal trajectory in the total parametric space that completes a self-consistency of those parameters belonging to ρ with those of a 'host' Ψ.

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