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Time-dependent tight binding

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Abstract

Starting from a Lagrangian mean-field theory, a set of time-dependent tight-binding equations is derived to describe dynamically and self-consistently an interacting system of quantum electrons and classical nuclei. These equations conserve norm, total energy and total momentum. A comparison with other tight-binding models is made. A previous tight-binding result for forces on atoms in the presence of electrical current flow is generalized to the time-dependent domain and is taken beyond the limit of local charge neutrality.

1. Introduction

The purpose of the derivations below is to obtain a set of time-dependent (TD) tight-binding (TB) equations, describing dynamically and self-consistently an interacting system of quantum electrons and moving classical nuclei. A general TD form of TB may have a range of applications. Processes where a dynamical coupling between electrons and nuclei is of interest include excitations in clusters [1] and the mechanical response of a small conductor to current-induced forces and local heating under electrical current flow [2, 3]. A third example is the propagation of an electron–hole pair in a long molecule and the structural response of the molecule. A further purpose of the present work is to recover a TB expression for interatomic forces in the presence of electrical current flow, obtained previously from a steady-state statistical point of view [2].

The derivation of the TD TB equations starts from a Lagrangian one-electron mean-field theory in the spirit of TD density-functional theory (DFT) [4, 5]. The derivation proceeds by an exact rearrangement of the *ab initio* Lagrangian, followed by the introduction of an atomic orbital basis set. This results in a system of one-particle TD Schrödinger equations (SE) for the electrons, coupled self-consistently with Newtonian equations of motion for the nuclei, with a TB structure. These equations conserve the norm of one-electron states, and the total energy and momentum of the system of electrons and nuclei. The form of these equations allows a range of TB models, from *ab initio* to empirical ones, to be discussed within a common framework. The example of a single-orbital orthogonal TB model with second-order Coulomb interactions is discussed in detail. In the limit of local charge neutrality, an earlier expression for current-induced forces [2] is recovered.

The most closely related work of which the author is aware is the TD TB scheme in reference [6] and the *ab initio* TD TB scheme in reference [7]. The dynamical equations in those works differ from the ones found here. A particular difference is the appearance, in the present paper, of terms in the Newtonian forces on nuclei that depend on the nuclear velocities. These terms disappear identically in the case of a complete basis set. In the case of an incomplete basis set, these terms are needed to conserve the total momentum of the system.

The next section describes the dynamical picture of an interacting system of quantum electrons and classical nuclei, on which the paper is based. Section 3 introduces the TD mean-field theory, from which the TD TB equations are to be derived. Section 4 expresses this mean-field theory in a general basis set that depends parametrically on the nuclear positions. In section 5, the TD TB equations are obtained as a special case of the previous section. The formalism is extended to simplified empirical TB models. An orthogonal TB model with second-order Coulomb interactions is discussed in section 6. The last section contains a summary of the main results of the paper.

2. Lagrangian semiclassical dynamics

We consider a system of N_e quantum electrons and N_z classical nuclei. A dynamical description of such a system is afforded by the equations

$$E = \langle \Psi_e(t) | \mathcal{H} | \Psi_e(t) \rangle + \sum_{n=1}^{N_z} [\mathbf{P}_n(t)]^2 / 2M_n + \phi[\{\mathbf{R}_n(t)\}] \quad (1)$$

$$\mathcal{H} | \Psi_e(t) \rangle = i\hbar | \dot{\Psi}_e(t) \rangle \quad \mathcal{H} = \sum_{i=1}^{N_e} \hat{\mathbf{p}}_i^2 / 2m_e + \sum_{n=1}^{N_z} \int \hat{\rho}(\mathbf{r}) v_n[\mathbf{r} - \mathbf{R}_n(t)] d\mathbf{r} + W(\{\hat{\mathbf{r}}_i\}) \quad (2)$$

$$\dot{\mathbf{R}}_n(t) = \mathbf{P}_n(t) / M_n \quad (3)$$

$$\dot{\mathbf{P}}_n(t) = - \int \rho(\mathbf{r}, t) \nabla_n v_n[\mathbf{r} - \mathbf{R}_n(t)] d\mathbf{r} - \nabla_n \phi \quad \rho(\mathbf{r}, t) = \langle \Psi_e(t) | \hat{\rho}(\mathbf{r}) | \Psi_e(t) \rangle. \quad (4)$$

Here, E is the total energy of the system. $|\Psi_e(t)\rangle$ is a N_e -particle fermionic state-vector, describing the electrons. $\mathbf{R}_n(t)$, $\mathbf{P}_n(t)$ and M_n are the position, momentum and mass of nucleus n , respectively. ϕ is the nucleus–nucleus interaction, W is the electron–electron interaction and v_n is the interaction potential between an electron and nucleus n . $\hat{\mathbf{r}}_i = (\hat{r}_{ix}, \hat{r}_{iy}, \hat{r}_{iz})$ and $\hat{\mathbf{p}}_i = (\hat{p}_{ix}, \hat{p}_{iy}, \hat{p}_{iz})$ are electron position and momentum operators, respectively, with $[\hat{r}_{i\mu}, \hat{p}_{j\nu}] = i\hbar \delta_{ij} \delta_{\mu\nu}$. $\hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N_e} \delta(\mathbf{r} - \hat{\mathbf{r}}_i)$ is the electron number-density operator and m_e is the electron mass. Throughout the paper, $\dot{F} = dF/dt$ and $\ddot{F} = d^2F/dt^2$, for any function of time $F = F(t)$. Throughout the paper, $\nabla_n = (\partial/\partial R_{nx}, \partial/\partial R_{ny}, \partial/\partial R_{nz})$ with $\mathbf{R}_n = \mathbf{R}_n(t) = (R_{nx}, R_{ny}, R_{nz})$. Everywhere, indices i and j refer to electrons and index n refers to nuclei. From now on, the limits in summations over these indices will be omitted, on the understanding that in such summations i and j run from 1 to N_e , and n runs from 1 to N_z .

Equation (4) may be deduced from equations (1), (2) and (3) under the assumption of total-energy conservation [7]. Such a deduction contains an additional assumption that needs to be shown explicitly for our purposes here. Let us assume equations (1), (2) and (3) and let us allow the system to evolve through an infinitesimal time increment dt . We find

$$dE/dt = \sum_n \dot{\mathbf{R}}_n(t) \cdot \left(\int \rho(\mathbf{r}, t) \nabla_n v_n[\mathbf{r} - \mathbf{R}_n(t)] d\mathbf{r} + \dot{\mathbf{P}}_n(t) + \nabla_n \phi \right). \quad (5)$$

We now make the additional assumption that, at any time t , the acceleration of each nucleus, $\dot{\mathbf{P}}_n(t)/M_n$, depends only on the instantaneous $|\Psi_e(t)\rangle$ and $\{\mathbf{R}_n(t)\}$, and is independent of the

nuclear velocities, $\{\dot{\mathbf{R}}_n(t)\}$. Then the expression in the large brackets above is independent of $\{\dot{\mathbf{R}}_n(t)\}$. Hence, by imposing $dE/dt = 0$, we force this expression to vanish. This yields equation (4). We will refer to this, and analogous Newtonian equations of motion, generically as the Hellmann–Feynman (HF) theorem. The assumption that the nuclear accelerations are independent of the nuclear velocities is plausible here. However, as will be shown in section 4, this assumption need not hold in the case of an incomplete basis set.

Equations (1), (2), (3) and (4) may be derived from a fully quantum picture [7–10]. A justification for these equations, starting from first principles, is given in appendix 1. These equations may also be derived from the Lagrangian [9, 11, 12]

$$L = i\hbar \langle \Psi_e(t) | \dot{\Psi}_e(t) \rangle - \langle \Psi_e(t) | \mathcal{H} | \Psi_e(t) \rangle + \sum_n M_n [\dot{\mathbf{R}}_n(t)]^2 / 2 - \phi[\{\mathbf{R}_n(t)\}]. \quad (6)$$

To do this, we write $|\Psi_e(t)\rangle = \sum_\alpha \psi_\alpha(t) |\alpha\rangle$ and $|\dot{\Psi}_e(t)\rangle = \sum_\alpha \dot{\psi}_\alpha(t) |\alpha\rangle$, where $\{|\alpha\rangle\}$ is an arbitrary complete orthonormal time-independent many-electron basis. L becomes¹

$$\begin{aligned} L &= L[\{\psi_\alpha\}, \{\dot{\psi}_\alpha\}, \{\psi_\alpha^*\}, \{\dot{\psi}_\alpha^*\}, \{\mathbf{R}_n\}, \{\dot{\mathbf{R}}_n\}] \\ &= i\hbar \sum_\alpha \psi_\alpha^* \dot{\psi}_\alpha - \sum_{\alpha, \alpha'} \psi_\alpha^* \mathcal{H}_{\alpha\alpha'} \psi_{\alpha'} + \sum_n M_n \dot{\mathbf{R}}_n^2 / 2 - \phi(\{\mathbf{R}_n\}) \end{aligned} \quad (7)$$

where $\psi_\alpha = \psi_\alpha(t)$, $\mathbf{R}_n = \mathbf{R}_n(t)$ and $\mathcal{H}_{\alpha\alpha'} = \langle \alpha | \mathcal{H} | \alpha' \rangle$. We demand that the action $S = \int_{t_0}^{t_1} L dt$ is stationary under an arbitrary variation $\psi_\alpha(t) \rightarrow \psi_\alpha(t) + \delta\psi_\alpha(t)$, $\mathbf{R}_n(t) \rightarrow \mathbf{R}_n(t) + \delta\mathbf{R}_n(t)$, with $\delta\psi_\alpha(t_0) = \delta\psi_\alpha(t_1) = 0$, $\delta\mathbf{R}_n(t_0) = \delta\mathbf{R}_n(t_1) = 0$. This yields the Lagrangian equations of motion²

$$\partial L / \partial \psi_\alpha - (d/dt)(\partial L / \partial \dot{\psi}_\alpha) = 0 \quad (8)$$

$$\partial L / \partial \psi_\alpha^* - (d/dt)(\partial L / \partial \dot{\psi}_\alpha^*) = 0 \quad (9)$$

$$\partial L / \partial \mathbf{R}_n - (d/dt)(\partial L / \partial \dot{\mathbf{R}}_n) = 0. \quad (10)$$

Throughout the paper, for any vector $\mathbf{a} = (a_x, a_y, a_z)$, $\partial/\partial\mathbf{a}$ is used as alternative notation for the gradient operator with respect to \mathbf{a} , $\partial/\partial\mathbf{a} = (\partial/\partial a_x, \partial/\partial a_y, \partial/\partial a_z)$. Equation (9) gives the TD SE:

$$i\hbar \dot{\psi}_\alpha(t) = \sum_{\alpha'} \mathcal{H}_{\alpha\alpha'} \psi_{\alpha'}(t). \quad (11)$$

This is equation (2) in matrix form. Equation (8) gives the complex conjugate of equation (11). The TD SE conserves the norm of $|\Psi_e(t)\rangle$. Therefore, it is not necessary to impose norm-conservation as an explicit constraint in the variational procedure above. Equation (10) gives $M_n \ddot{\mathbf{R}}_n(t) = - \sum_{\alpha, \alpha'} \psi_\alpha^*(t) (\nabla_n \mathcal{H}_{\alpha\alpha'}) \psi_{\alpha'}(t) - \nabla_n \phi$

$$= - \int \rho(\mathbf{r}, t) \nabla_n v_n[\mathbf{r} - \mathbf{R}_n(t)] d\mathbf{r} - \nabla_n \phi. \quad (12)$$

The momentum conjugate to $\mathbf{R}_n(t)$ is given by

$$\mathbf{P}_n(t) = \partial L / \partial \dot{\mathbf{R}}_n = M_n \dot{\mathbf{R}}_n(t). \quad (13)$$

The total energy of the system is given by the Legendre transformation

$$E = \sum_\alpha \dot{\psi}_\alpha (\partial L / \partial \dot{\psi}_\alpha) + \sum_{\alpha'} \dot{\psi}_{\alpha'}^* (\partial L / \partial \dot{\psi}_{\alpha'}^*) + \sum_n \dot{\mathbf{R}}_n \cdot (\partial L / \partial \dot{\mathbf{R}}_n) - L \quad (14)$$

$$= \sum_{\alpha, \alpha'} \psi_\alpha^*(t) \mathcal{H}_{\alpha\alpha'} \psi_{\alpha'}(t) + \sum_n [\mathbf{P}_n(t)]^2 / 2M_n + \phi[\{\mathbf{R}_n(t)\}]. \quad (15)$$

¹ In the present case $\dot{\psi}_\alpha^*$ does not appear in L , but it is accommodated in the formalism for generality.

² In this variational procedure, the real and imaginary parts of ψ_α must be treated as independent variables. This is equivalent to treating ψ_α and ψ_α^* as independent variables [12], which yields the Euler–Lagrange equations in the text.

Equations (11), (12), (13) and (15) are the same as equations (2), (4), (3) and (1), respectively. The Lagrangian approach will be used later to derive the TD TB equations. Three points are now addressed in connection with the above equations of motion in order to specify the underlying assumptions and scope of the paper.

The first point concerns the boundary conditions with which the equations of motion are to be integrated. In semiclassical theories of collision processes, there are methods in which one imposes requirements on the state-vector of the quantum subsystem both at some initial time and at some final time, in order for instance to describe a particular excitation [13, 14]. This is not done here. Instead, here we imagine that the evolution of the system is to be determined by a set of initial conditions, specifying the nuclear positions and velocities, and, up to an arbitrary phase factor, the electron state-vector, at some initial time t_0 . Integration of equations (2), (3) and (4) then produces unique values for $\{\mathbf{R}_n(t)\}$ and $|\Psi_e(t)\rangle$ for any $t > t_0$.

The second point concerns the physical interpretation of the equations of motion. For a given set of initial conditions, equations (2), (3) and (4) produce a unique set of classical nuclear trajectories. The motion of the electrons, on the other hand, is governed by quantum mechanics. Within the standard probabilistic interpretation of quantum mechanics, at any time the electron state-vector $|\Psi_e(t)\rangle$ harbours a statistical distribution of possible outcomes of a measurement on the electron subsystem [15]. This mixed deterministic–probabilistic description, in which all of these possible outcomes are associated with a single set of classical nuclear trajectories, may become an issue in situations in which one wishes to describe an individual transition of the quantum subsystem [13, 16]. This issue will not be pursued here. Instead, here we observe that, via $|\Psi_e(t)\rangle$, for a given set of initial conditions, equations (2), (3) and (4) give an unambiguous result for the statistical distribution as a whole, and for the expectation value in particular, of any quantum-mechanical electronic operator, at any time t . Therefore, in cases where this statistical distribution, or expectation value, is in itself physically meaningful, these equations produce a meaningful result. Two examples of such cases are the instantaneous electron density, $\rho(\mathbf{r}, t) = \langle \Psi_e(t) | \hat{\rho}(\mathbf{r}) | \Psi_e(t) \rangle$, and the electron current density, $\mathbf{j}(\mathbf{r}, t) = \langle \Psi_e(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Psi_e(t) \rangle$, where $\hat{\mathbf{j}}(\mathbf{r})$ is the electron current-density operator. Both of these quantities are used in the theory of atoms, molecules and solids, with applications to bonding, structure and transport. In this paper, we proceed on the understanding that if in a given problem the above mixed deterministic–probabilistic description is a cause for concern, then in that problem the use of the electron state-vector is to be restricted to the calculation of statistical properties and expectation values.

The third point concerns the validity of the classical description of the nuclei [8]. The argument in appendix 1 is valid in the limits of high nuclear masses or high nuclear energies, where each nucleus can be localized sufficiently, both in real space and in momentum space [8]. For molecules and solids these requirements are very restrictive. A further limitation of equations (2), (3) and (4)—that of the mixed deterministic–probabilistic description and its applicability to individual excitations [7, 13, 16]—was mentioned above. The classical description of nuclei is also restrictive physically. Examples of phenomena in which the quantum nature of nuclei is apparent are tunnelling of light nuclei in solids, the behaviour of the phonon heat capacity at low temperatures and zero-point motion. Nonetheless, the classical description of nuclei is widely used in static and in dynamical calculations, in TB [17] and in DFT [1]. The range of validity of the classical description of nuclei [8] is not a subject of this paper. The question considered here is: if we assume this description, then what is the appropriate form of the equations of motion in a one-electron mean-field picture, in an approximate basis set?

Subject to the above provisos, equations (2), (3) and (4) define a dynamical description of a system of electrons and nuclei. Within this description, electrons can be in a non-stationary

state. The above equations then allow a dynamical exchange of momentum and energy between electrons and nuclei [5, 7, 9]. An example of a dynamical process, that will be referred to in the paper, is the evolution towards equilibrium of an initial non-equilibrium electron charge distribution in a conductor.

3. Time-dependent mean-field theory

So far, the description of the electrons contained the full many-body electron–electron interaction W in equation (2). We now replace the energy of this interaction, at any time t , by a functional, $\mathcal{E}_{hxc} = \mathcal{E}_{hxc}[\rho]$, of the instantaneous electron density $\rho = \rho(\mathbf{r}, t)$. We will not consider spin-dependent interactions. The choice of \mathcal{E}_{hxc} is a specification of the model. Within the Hartree approximation, \mathcal{E}_{hxc} would be given by the Hartree energy. In a better approximation, \mathcal{E}_{hxc} might be given by the Hartree energy plus the exchange–correlation energy, calculated from ground-state DFT in the local density approximation [1, 5]. Here, we treat $\mathcal{E}_{hxc}[\rho]$ as a general differentiable model functional. Next, we take the electrons to be described by a set of one-particle states, satisfying a one-particle TD SE with an effective potential $V = \sum_n v_n + v_{hxc}$, where $v_{hxc} = \delta\mathcal{E}_{hxc}/\delta\rho$. Justification for such a one-electron description may be sought in TD DFT [1, 4, 5]. Alternatively, this description may be viewed as an empirical TD mean-field theory.

The dynamical equations of the theory may be obtained from the Lagrangian [5]

$$L = i\hbar \sum_i \langle \psi_i(t) | \dot{\psi}_i(t) \rangle - \sum_i \langle \psi_i(t) | \hat{T} | \psi_i(t) \rangle - \mathcal{E}[\rho] + \sum_n M_n [\dot{\mathbf{R}}_n(t)]^2 / 2 - \phi[\{\mathbf{R}_n(t)\}] \quad (16)$$

where

$$\mathcal{E}[\rho] = \sum_n \int \rho(\mathbf{r}, t) v_n[\mathbf{r} - \mathbf{R}_n(t)] d\mathbf{r} + \mathcal{E}_{hxc}[\rho] \quad (17)$$

$$\rho = \rho(\mathbf{r}, t) = \sum_i |\psi_i(\mathbf{r}, t)|^2. \quad (18)$$

Here, $\{|\psi_i(t)\rangle\}$ is a set of N_e normalizable one-particle states, one for each electron in the system, and $\psi_i(\mathbf{r}, t) = \langle \mathbf{r} | \psi_i(t) \rangle$. $\hat{T} = \hat{\mathbf{p}}^2/2m_e$ is the one-electron kinetic energy operator, where $\hat{\mathbf{p}}$ is the one-particle momentum operator. We recall the property $\langle \mathbf{r} | \hat{\mathbf{p}} | \mathbf{r}' \rangle = -i\hbar \nabla \delta(\mathbf{r} - \mathbf{r}')$. Throughout the paper, $\nabla = (\partial/\partial x, \partial/\partial y, \partial/\partial z)$ with $\mathbf{r} = (x, y, z)$. Everywhere, $\langle \eta | \zeta \rangle = \int \langle \eta | \mathbf{r} \rangle d\mathbf{r} \langle \mathbf{r} | \zeta \rangle$ for any two one-electron states $|\eta\rangle$ and $|\zeta\rangle$.

We follow the Lagrangian variational procedure in section 2. We write

$$|\psi_i(t)\rangle = \sum_{\zeta} \psi_{i\zeta}(t) |\zeta\rangle \quad |\dot{\psi}_i(t)\rangle = \sum_{\zeta} \dot{\psi}_{i\zeta}(t) |\zeta\rangle$$

where $\{|\zeta\rangle\}$ is an arbitrary complete orthonormal time-independent one-electron basis. L becomes

$$L = L(\{\psi_{i\zeta}\}, \{\dot{\psi}_{i\zeta}\}, \{\psi_{i\zeta}^*\}, \{\dot{\psi}_{i\zeta}^*\}, \{\mathbf{R}_n\}, \{\dot{\mathbf{R}}_n\}) \\ = i\hbar \sum_{i,\zeta} \psi_{i\zeta}^* \dot{\psi}_{i\zeta} - \sum_{i,\zeta,\zeta'} \psi_{i\zeta}^* T_{\zeta\zeta'} \psi_{i\zeta'} - \mathcal{E}[\rho] + \sum_n M_n \dot{\mathbf{R}}_n^2 / 2 - \phi(\{\mathbf{R}_n\}) \quad (19)$$

where $\psi_{i\zeta} = \psi_{i\zeta}(t)$, $\mathbf{R}_n = \mathbf{R}_n(t)$, $T_{\zeta\zeta'} = \langle \zeta | \hat{T} | \zeta' \rangle$ and

$$\rho = \rho(\mathbf{r}, t) = \sum_{i,\zeta,\zeta'} \psi_{i\zeta}^*(t) \langle \zeta | \mathbf{r} \rangle \langle \mathbf{r} | \zeta' \rangle \psi_{i\zeta'}(t).$$

A stationary-action requirement now gives equations (8), (9) and (10), with ψ_α and ψ_α^* replaced by $\psi_{i\zeta}$ and $\psi_{i\zeta}^*$, respectively. Equation (9) yields the one-electron TD SE

$$i\hbar\dot{\psi}_{i\zeta}(t) = \sum_{\zeta'} H_{\zeta\zeta'}\psi_{i\zeta'}(t) \quad (20)$$

where

$$H_{\zeta\zeta'} = \langle \zeta | \hat{H} | \zeta' \rangle \quad \hat{H} = \hat{T} + \hat{V} \quad \hat{V} = \int |\mathbf{r}\rangle V(\mathbf{r}, t) \langle \mathbf{r}| d\mathbf{r} \quad (21)$$

$$V(\mathbf{r}, t) = \delta\mathcal{E}[\rho]/\delta\rho = \sum_n v_n[\mathbf{r} - \mathbf{R}_n(t)] + v_{hxc}(\mathbf{r}, t) \quad v_{hxc}(\mathbf{r}, t) = \delta\mathcal{E}_{hxc}[\rho]/\delta\rho. \quad (22)$$

Equation (8) gives the complex conjugate of equation (20). In evaluating equations (8) and (9), we have used the relation

$$\begin{aligned} \partial\mathcal{E}/\partial\psi_{i\zeta}^* &= \int (\delta\mathcal{E}/\delta\rho)(\partial\rho/\partial\psi_{i\zeta}^*) d\mathbf{r} \\ &= \sum_{\zeta'} \int \langle \zeta | \mathbf{r} \rangle V(\mathbf{r}, t) \langle \mathbf{r} | \zeta' \rangle \psi_{i\zeta'}(t) d\mathbf{r} = \sum_{\zeta'} \langle \zeta | \hat{V} | \zeta' \rangle \psi_{i\zeta'}(t) = (\partial\mathcal{E}/\partial\psi_{i\zeta})^*. \end{aligned} \quad (23)$$

Equation (20) may also be written in operator form as $i\hbar|\dot{\psi}_i(t)\rangle = \hat{H}|\psi_i(t)\rangle$. Equation (10) gives the HF theorem

$$M_n\ddot{\mathbf{R}}_n(t) = - \int \rho(\mathbf{r}, t) \nabla_n v_n[\mathbf{r} - \mathbf{R}_n(t)] d\mathbf{r} - \nabla_n\phi. \quad (24)$$

For the energy of the system, a Legendre transformation as in equation (14) gives

$$E = \sum_i \langle \psi_i(t) | \hat{T} | \psi_i(t) \rangle + \mathcal{E}[\rho] + \sum_n M_n[\dot{\mathbf{R}}_n(t)]^2/2 + \phi[\{\mathbf{R}_n(t)\}]. \quad (25)$$

These equations satisfy the following conservation laws [5]. The TD SE conserves the inner product $\langle \psi_i(t) | \psi_j(t) \rangle$. Hence, it is not necessary to impose orthonormality as an explicit constraint in the Lagrangian variational procedure. Since L has no explicit time dependence, E is a constant of the motion [18]. It may be verified explicitly from equations (20), (24) and (25) that $\dot{E} = 0$. Finally, the total momentum of the electrons and nuclei is conserved. Indeed, let

$$\mathbf{P}_e(t) = \sum_i \langle \psi_i(t) | \hat{\mathbf{p}} | \psi_i(t) \rangle. \quad (26)$$

Then

$$\begin{aligned} \dot{\mathbf{P}}_e(t) &= (1/i\hbar) \sum_i \langle \psi_i(t) | [\hat{\mathbf{p}}, \hat{H}] | \psi_i(t) \rangle \\ &= (1/i\hbar) \sum_i \langle \psi_i(t) | [\hat{\mathbf{p}}, \hat{V}] | \psi_i(t) \rangle = \int V(\mathbf{r}, t) \nabla \rho(\mathbf{r}, t) d\mathbf{r}. \end{aligned} \quad (27)$$

But $\mathcal{E}[\rho] = \sum_n \int \rho(\mathbf{r}, t) v_n[\mathbf{r} - \mathbf{R}_n(t)] d\mathbf{r} + \mathcal{E}_{hxc}[\rho]$ is invariant under the transformation $\rho(\mathbf{r}, t) \rightarrow \rho(\mathbf{r} - \mathbf{\Delta}, t)$, $\{\mathbf{R}_n(t)\} \rightarrow \{\mathbf{R}_n(t) + \mathbf{\Delta}\}$, for any $\mathbf{\Delta}$. Hence,

$$\begin{aligned} & - \int (\nabla \rho)(\delta\mathcal{E}/\delta\rho) d\mathbf{r} + \sum_n \int \rho(\mathbf{r}, t) \nabla_n v_n[\mathbf{r} - \mathbf{R}_n(t)] d\mathbf{r} \\ &= - \int V(\mathbf{r}, t) \nabla \rho(\mathbf{r}, t) d\mathbf{r} + \sum_n \int \rho(\mathbf{r}, t) \nabla_n v_n[\mathbf{r} - \mathbf{R}_n(t)] d\mathbf{r} = 0. \end{aligned} \quad (28)$$

Furthermore, $\phi[\{\mathbf{R}_n(t)\}]$ is invariant under rigid translations of the nuclei as a whole, and hence $\sum_n \nabla_n \phi = 0$. It follows that

$$\dot{\mathbf{P}}_e(t) + \sum_n M_n \ddot{\mathbf{R}}_n(t) = 0. \quad (29)$$

4. Mean-field theory in a parametric basis set

The TD mean-field theory of the previous section is now to be expressed in a general basis $\{|\beta\rangle\}$, where each basis state, $|\beta\rangle = |\beta[\{\mathbf{R}_n(t)\}]\rangle$, depends parametrically on the nuclear positions $\{\mathbf{R}_n(t)\}$. The basis $\{|\beta\rangle\}$ may be complete or incomplete. In general, it may contain a discrete and a continuum part. The basis states may be non-orthogonal. The only requirement that we impose is that, for any Δ , $\beta[\mathbf{r}, \{\mathbf{R}_n(t)\}] = \langle \mathbf{r} | \beta \rangle$ satisfies $\beta[\mathbf{r}, \{\mathbf{R}_n(t) + \Delta\}] = \beta[\mathbf{r} - \Delta, \{\mathbf{R}_n(t)\}]$, or

$$\nabla \beta[\mathbf{r}, \{\mathbf{R}_n(t)\}] + \sum_n \nabla_n \beta[\mathbf{r}, \{\mathbf{R}_n(t)\}] = 0. \quad (30)$$

We now write

$$|\psi_i(t)\rangle = \sum_{\beta} \psi_{i\beta}(t) |\beta\rangle \quad (31)$$

$$|\dot{\psi}_i(t)\rangle = \sum_{\beta} [\dot{\psi}_{i\beta}(t) |\beta\rangle + \psi_{i\beta}(t) |\dot{\beta}\rangle] \quad (32)$$

where

$$|\dot{\beta}\rangle = \sum_n |\nabla_n \beta\rangle \cdot \dot{\mathbf{R}}_n(t). \quad (33)$$

Here, $|\nabla_n \beta\rangle$ is defined by $\langle \mathbf{r} | \nabla_n \beta \rangle = \nabla_n \langle \mathbf{r} | \beta \rangle$. The electron density in equation (18) is now given by

$$\begin{aligned} \rho = \rho(\mathbf{r}, t) &= \sum_{i, \beta, \beta'} \psi_{i\beta}^*(t) \langle \beta | \mathbf{r} \rangle \langle \mathbf{r} | \beta' \rangle \psi_{i\beta'}(t) \\ &= \sum_{i, \beta, \beta'} \psi_{i\beta}^*(t) \beta^*[\mathbf{r}, \{\mathbf{R}_n(t)\}] \beta'[\mathbf{r}, \{\mathbf{R}_n(t)\}] \psi_{i\beta'}(t). \end{aligned} \quad (34)$$

Equation (31) is more than just an expansion. If $\{|\beta\rangle\}$ is incomplete, then by writing this equation we impose a constraint on the electron states $\{|\psi_i(t)\rangle\}$. This constraint is that these states now lie in that subspace of the original Hilbert space, which is spanned by the basis $\{|\beta\rangle\}$. Since the basis states $\{|\beta\rangle\}$ depend on the nuclear positions, this subspace will in general vary with time. A classical analogue of this constraint would be to restrict the trajectories of the electrons in a way that is itself tied up with the motion of the nuclei. For example, the electrons might be constrained to slide frictionlessly along a set of massless wires, with the wires themselves attached to the moving nuclei.

4.1. Lagrangian equations of motion

Equations (31) and (32) are substituted into the Lagrangian from equation (16). This gives

$$\begin{aligned} L &= L(\{\psi_{i\beta}\}, \{\dot{\psi}_{i\beta}\}, \{\psi_{i\beta}^*\}, \{\dot{\psi}_{i\beta}^*\}, \{\mathbf{R}_n\}, \{\dot{\mathbf{R}}_n\}) \\ &= i\hbar \sum_{i, \beta, \beta'} \psi_{i\beta}^* \langle \beta | \dot{\beta}' \rangle \psi_{i\beta'} + i\hbar \sum_{i, \beta, \beta'} \dot{\psi}_{i\beta}^* \langle \beta | \beta' \rangle \psi_{i\beta'} - \sum_{i, \beta, \beta'} \psi_{i\beta}^* T_{\beta\beta'} \psi_{i\beta'} - \mathcal{E}[\rho] \\ &\quad + \sum_n M_n \dot{\mathbf{R}}_n^2 / 2 - \phi(\{\mathbf{R}_n\}) \end{aligned} \quad (35)$$

where $\psi_{i\beta} = \psi_{i\beta}(t)$, $\mathbf{R}_n = \mathbf{R}_n(t)$, $T_{\beta\beta'} = \langle \beta | \hat{T} | \beta' \rangle$ and ρ is given by equation (34).

The Lagrangian equations of motion are now given by equations (8), (9) and (10), with ψ_{α} and ψ_{α}^* replaced by $\psi_{i\beta}$ and $\psi_{i\beta}^*$, respectively. Equation (9) yields the TD SE

$$i\hbar \sum_{\beta'} \langle \beta | \dot{\beta}' \rangle \psi_{i\beta'}(t) + i\hbar \sum_{\beta'} \langle \beta | \beta' \rangle \dot{\psi}_{i\beta'}(t) = \sum_{\beta'} H_{\beta\beta'} \psi_{i\beta'}(t) \quad (36)$$

where $H_{\beta\beta'} = \langle \beta | \hat{H} | \beta' \rangle$. Here, once again, $\hat{H} = \hat{T} + \hat{V}$, $\hat{V} = \int |\mathbf{r}\rangle V(\mathbf{r}, t) \langle \mathbf{r}| d\mathbf{r}$ and $V(\mathbf{r}, t) = \delta\mathcal{E}[\rho]/\delta\rho$, with ρ now given by equation (34). In deriving equation (36) we have used the analogue, in the present case, of equation (23). Equation (8) gives the complex conjugate of equation (36).

To evaluate equation (10) we should note that now L depends on the nuclear velocities both via the nuclear kinetic energy term and via the quantity

$$\langle \beta | \dot{\beta}' \rangle = \sum_n \langle \beta | \nabla_n \beta' \rangle \cdot \dot{\mathbf{R}}_n(t). \quad (37)$$

We must remember also that $\langle \beta | \beta' \rangle$, $\langle \beta | \dot{\beta}' \rangle$, $\langle \beta | \nabla_n \beta' \rangle$ and $T_{\beta\beta'}$ all depend on $\{\mathbf{R}_n(t)\}$, via the dependence on $\{\mathbf{R}_n(t)\}$ of the basis states $\{|\beta\rangle\}$. Equation (10), together with (36), gives the HF theorem

$$\begin{aligned} M_n \dot{\mathbf{R}}_n(t) = & -\nabla_n \mathcal{E} - \nabla_n \phi - \sum_{i,\beta,\beta'} \psi_{i\beta}^*(t) (\nabla_n T_{\beta\beta'}) \psi_{i\beta'}(t) \\ & + \sum_{i,\beta,\beta',\beta'',\beta'''} [\psi_{i\beta}^*(t) \langle \nabla_n \beta | \beta' \rangle S_{\beta'\beta''}^{-1} H_{\beta''\beta'''} \psi_{i\beta'''}(t) + \text{c.c.}] \\ & + i\hbar \sum_{i,\beta,\beta'} [\psi_{i\beta}^*(t) \langle \nabla_n \beta | \dot{\beta}' \rangle \psi_{i\beta'}(t) - \text{c.c.}] \\ & - i\hbar \sum_{i,\beta,\beta',\beta'',\beta'''} [\psi_{i\beta}^*(t) \langle \nabla_n \beta | \beta' \rangle S_{\beta'\beta''}^{-1} \langle \beta'' | \dot{\beta}''' \rangle \psi_{i\beta'''}(t) - \text{c.c.}] \end{aligned} \quad (38)$$

where $\nabla_n \mathcal{E} = (\partial \mathcal{E} / \partial \mathbf{R}_n)_{\{\psi_{i\beta}\}, \{\psi_{i\beta}^*\}, \{\mathbf{R}_{m \neq n}\}}$ and $z \pm \text{c.c.} = z \pm z^*$ for any complex number z . Above we have introduced the Hermitian overlap matrix $S_{\beta\beta'} = \langle \beta | \beta' \rangle$ and we have assumed that it is invertible. $\mathcal{E}[\rho]$ depends on $\{\mathbf{R}_n(t)\}$ both via $\{v_n[\mathbf{r} - \mathbf{R}_n(t)]\}$ and via $\{\beta[\mathbf{r}, \{\mathbf{R}_n(t)\}]\}$ in equation (34). Hence, in equation (38)

$$\begin{aligned} \nabla_n \mathcal{E} = & (\partial \mathcal{E} / \partial \mathbf{R}_n)_{\{\psi_{i\beta}\}, \{\psi_{i\beta}^*\}, \{\mathbf{R}_{m \neq n}\}} \\ = & \int \rho(\mathbf{r}, t) \nabla_n v_n[\mathbf{r} - \mathbf{R}_n(t)] d\mathbf{r} \\ & + \sum_{i,\beta,\beta'} \psi_{i\beta}^*(t) (\langle \nabla_n \beta | \hat{V} | \beta' \rangle + \langle \beta | \hat{V} | \nabla_n \beta' \rangle) \psi_{i\beta'}(t). \end{aligned} \quad (39)$$

The energy of the system is given by the Legendre transformation

$$\begin{aligned} E = & \sum_{i,\beta} \dot{\psi}_{i\beta} (\partial L / \partial \dot{\psi}_{i\beta}) + \sum_{i,\beta} \dot{\psi}_{i\beta}^* (\partial L / \partial \dot{\psi}_{i\beta}^*) + \sum_n \dot{\mathbf{R}}_n \cdot (\partial L / \partial \dot{\mathbf{R}}_n) - L \\ = & \sum_{i,\beta,\beta'} \psi_{i\beta}^*(t) T_{\beta\beta'} \psi_{i\beta'}(t) + \mathcal{E}[\rho] + \sum_n M_n [\dot{\mathbf{R}}_n(t)]^2 / 2 + \phi[\{\mathbf{R}_n(t)\}]. \end{aligned} \quad (40)$$

All terms in equation (38) that involve derivatives of the basis states $\{|\beta\rangle\}$ are Pulay-like forces [19]. If the basis $\{|\beta\rangle\}$ is complete, then these forces vanish identically. Indeed, if $\{|\beta\rangle\}$ is complete, then $\sum_{\beta,\beta'} \langle \mathbf{r} | \beta \rangle S_{\beta\beta'}^{-1} \langle \beta' | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}')$. Then the terms in the fourth line of equation (38) exactly cancel those in the third line, while the second line becomes $\sum_{i,\beta,\beta'} \psi_{i\beta}^*(t) (\langle \nabla_n \beta | \hat{H} | \beta' \rangle + \langle \beta | \hat{H} | \nabla_n \beta' \rangle) \psi_{i\beta'}(t)$. Writing $\nabla_n T_{\beta\beta'} = \langle \nabla_n \beta | \hat{T} | \beta' \rangle + \langle \beta | \hat{T} | \nabla_n \beta' \rangle$ and using equation (39), we recover equation (24).

4.2. Conserved quantities

The dynamical equations above conserve orthonormality, total energy and total momentum. Conservation of the inner product $\langle \psi_i(t) | \psi_j(t) \rangle = \sum_{\beta,\beta'} \psi_{i\beta}^*(t) \langle \beta | \beta' \rangle \psi_{j\beta'}(t)$ follows from

equation (36). Indeed,

$$\begin{aligned}
(d/dt) \sum_{\beta, \beta'} \psi_{i\beta}^*(t) \langle \beta | \beta' \rangle \psi_{j\beta'}(t) \\
&= \sum_{\beta, \beta'} [\dot{\psi}_{i\beta}^*(t) \langle \beta | \beta' \rangle \psi_{j\beta'}(t) \\
&\quad + \psi_{i\beta}^*(t) \langle \dot{\beta} | \beta' \rangle \psi_{j\beta'}(t) + \psi_{i\beta}^*(t) \langle \beta | \dot{\beta}' \rangle \psi_{j\beta'}(t) + \psi_{i\beta}^*(t) \langle \beta | \beta' \rangle \dot{\psi}_{j\beta'}(t)] \\
&= (1/i\hbar) \sum_{\beta, \beta'} [-\psi_{i\beta}^*(t) H_{\beta\beta'} \psi_{j\beta'}(t) + \psi_{i\beta}^*(t) H_{\beta\beta'} \psi_{j\beta'}(t)] = 0. \tag{41}
\end{aligned}$$

Hence, once again, it is not necessary to impose orthonormality as a separate constraint in the Lagrangian variational procedure. The terms in equation (36) involving time derivatives of the basis states are crucial for the last line in equation (41), and are therefore needed to conserve orthonormality.

Conservation of energy follows from the lack of explicit time dependence of L in equation (35) [18]. It may be verified explicitly from equations (36), (38) and (40) that $\dot{E} = 0$.

Conservation of momentum also follows from an invariance property of L . For given $\{\psi_{i\beta}\}$ and $\{\dot{\psi}_{i\beta}\}$, L is invariant under the transformation $\{\mathbf{R}_n\} \rightarrow \{\mathbf{R}_n + \mathbf{\Delta}\}$, for any $\mathbf{\Delta}$. Hence, $\sum_n \partial L / \partial \mathbf{R}_n = 0$. Then equation (10), together with (30) and (37), implies that

$$(d/dt) \sum_{i, \beta, \beta'} \psi_{i\beta}^*(t) \langle \beta | \hat{p} | \beta' \rangle \psi_{i\beta'}(t) + \sum_n M_n \ddot{\mathbf{R}}_n(t) = 0. \tag{42}$$

This is a statement of conservation of mechanical momentum, in the sense of equations (26) and (29). Equation (42) can be verified explicitly from equations (36) and (38). This is done in appendix 2. That derivation shows explicitly that if the basis $\{|\beta\rangle\}$ is incomplete, then the terms in equation (38), which involve time derivatives of the basis states, are needed for momentum conservation.

4.3. Alternative approaches

A feature of the present approach is the appearance in equations (36) and (38) of terms that depend on time derivatives of the basis states, and hence, via equation (33), on the instantaneous nuclear velocities. It was shown above that in general these terms are needed for norm conservation, in the sense of equation (41), and for momentum conservation, in the sense of equation (42). The present Lagrangian approach is now compared with other possible approaches.

An alternative procedure would be to put $\mathbf{P}_n = M_n \dot{\mathbf{R}}_n$ in equation (40), and to write $\dot{\mathbf{P}}_n = -\partial E / \partial \mathbf{R}_n$. Such a procedure would not be compatible with the present formalism. The reason is that, for any generalized coordinate q , the Hamiltonian equation of motion $\dot{p}_q = -\partial E / \partial q$ applies to the canonical momentum $p_q = \partial L / \partial \dot{q}$. In the present case, and in general [18], the canonical momentum conjugate to \mathbf{R}_n , $\partial L / \partial \dot{\mathbf{R}}_n$, is distinct from the mechanical momentum $M_n \dot{\mathbf{R}}_n$. If E and L are linked by the Legendre transformation in equation (40), and if the transformation from generalized coordinates (in this case $\{\psi_{i\beta}\}, \{\dot{\psi}_{i\beta}\}, \{\mathbf{R}_n\}$) and velocities (in this case $\{\dot{\psi}_{i\beta}\}, \{\dot{\psi}_{i\beta}^*\}, \{\dot{\mathbf{R}}_n\}$) to generalized coordinates and conjugate canonical momenta (in this case $\{\partial L / \partial \psi_{i\beta}\}, \{\partial L / \partial \dot{\psi}_{i\beta}\}, \{\partial L / \partial \dot{\mathbf{R}}_n\}$) is done consistently, then the Hamiltonian formalism and the Lagrangian formalism are equivalent [20].

A Lagrangian approach is used in the TD TB formalism in reference [6]. In that paper, a semiempirical Lagrangian is used that is different from L in equation (35). The resulting

dynamical equations are different from the present ones. In particular, the dynamical equations in reference [6] do not contain terms involving time derivatives of the basis states.

Another approach would be to deduce an equation of motion for the nuclei from the requirement of total-energy conservation. In such an approach, one might start from equations (36) and (40), allow the system to evolve through an infinitesimal time interval dt , and impose $dE/dt = 0$. Subject to the additional assumption, as outlined in section 2, that the nuclear accelerations are independent of the nuclear velocities, one would then arrive at an expression for $M_n \dot{\mathbf{R}}_n(t)$, given by just the first two lines in equation (38). This is the force expression found in reference [7]. It is easy to see why the velocity-dependent terms in the third and fourth lines in equation (38) are not captured by an energy-conservation argument. Let us take the scalar product of both sides of equation (38) with $\dot{\mathbf{R}}_n(t)$, and sum over n . Then, in view of equation (33), the contributions from the third and fourth lines in equation (38) vanish. Thus, the velocity-dependent forces in equation (38) do not contribute to the rate of change, $\sum_n M_n \dot{\mathbf{R}}_n(t) \cdot \dot{\mathbf{R}}_n(t)$, of the total nuclear kinetic energy. Stated differently, the total work done by these velocity-dependent forces is zero. Within the present Lagrangian approach, the assumption that the nuclear accelerations are independent of the nuclear velocities would not be justified in the first place.

Caution is called for in pronouncing one of these approaches correct and another one wrong. The use of an incomplete basis introduces an error. In reference [7], for example, this error would manifest itself at the level of equation (42). Here, this error forces the appearance of velocity-dependent Pulay-like forces. This error is like a bubble of air in a balloon filled with liquid: you try to expel it from one place, and it pops up in another. The advantage of the present first-principles Lagrangian approach is that it yields the above conservation laws naturally, without a need to impose them as external conditions.

5. Time-dependent tight binding

TD TB results from an exact rearrangement of the quantity \mathcal{E} in equation (17), combined with a particular choice of basis, namely an atomic orbital basis. The resultant TB equations have a useful form that allows a range of models—from *ab initio* to empirical ones, from the limit of strong electron–electron repulsion to the limit of non-interacting electrons—to be discussed within a common algebraic framework.

5.1. First-principles tight binding

Let us step back to section 3. We make the following modifications. For generality, the bare nuclei are replaced by ions, although one may equally well adhere to the all-electron description, considered so far. Now v_n in equation (17) is the ionic pseudopotential of ion n . ϕ in equation (16) is the ion–ion interaction potential. M_n , $\mathbf{R}_n(t)$ and $\dot{\mathbf{R}}_n(t)$ now designate the mass, position and velocity of ion n , respectively. The N_e electrons that appear explicitly in the theory are now the valence electrons, described by a set of N_e one-particle states $\{|\psi_i(t)\rangle\}$. The choice of $\mathcal{E}_{hxc}[\rho]$ in equation (17) is once again a specification of the theory.

Next, we imagine performing a self-consistent valence electron calculation for atom n in isolation, placed at position $\mathbf{R}_n(t)$. In this calculation the atom may be neutral, or it may be in some ionized state. Let this calculation produce a set of atomic orbitals $\{|\phi_{n\gamma}\rangle\}$ with occupation numbers $\{f_{n\gamma}\}$. Index γ labels the various orbitals on atom n . The numbers $\{f_{n\gamma}\}$ are constants. Let also

$$\tilde{\Omega} = \sum_i |\psi_i(t)\rangle \langle \psi_i(t)| \quad \rho = \rho(\mathbf{r}, t) = \langle \mathbf{r} | \tilde{\Omega} | \mathbf{r} \rangle \quad (43)$$

$$\tilde{\Omega}_n = \sum_{\gamma} |\phi_{n\gamma}\rangle f_{n\gamma} \langle \phi_{n\gamma}| \quad \rho_n = \rho_n[\mathbf{r} - \mathbf{R}_n(t)] = \langle \mathbf{r} | \tilde{\Omega}_n | \mathbf{r} \rangle \quad (44)$$

$$\tilde{\Omega}_0 = \sum_n \tilde{\Omega}_n \quad \rho_0 = \rho_0[\mathbf{r}, \{\mathbf{R}_n(t)\}] = \langle \mathbf{r} | \tilde{\Omega}_0 | \mathbf{r} \rangle = \sum_n \rho_n[\mathbf{r} - \mathbf{R}_n(t)]. \quad (45)$$

Here, ρ is the instantaneous density of the valence electrons in the system, ρ_n is the valence electron density of atom n in isolation and ρ_0 is a rigid superposition of atomic valence electron densities.

We now write the quantity $\mathcal{E}[\rho]$ in equation (17) as

$$\begin{aligned} \mathcal{E}[\rho] &= \mathcal{E}[\rho_0] + \int \{\rho(\mathbf{r}, t) - \rho_0[\mathbf{r}, \{\mathbf{R}_n(t)\}]\} V_0(\mathbf{r}, t) \, d\mathbf{r} + \mathcal{E}^{TB}[\rho] \\ V_0(\mathbf{r}, t) &= (\delta\mathcal{E}/\delta\rho)_{\rho=\rho_0}. \end{aligned} \quad (46)$$

V_0 is the effective potential V in equation (22), evaluated at electron density ρ_0 . The density functional $\mathcal{E}^{TB}[\rho]$ is defined by equation (46). If $\mathcal{E}^{TB}[\rho]$ has a convergent Taylor expansion, then it may be approximated by a finite series in powers of $\Delta\rho(\mathbf{r}, t) = \rho(\mathbf{r}, t) - \rho_0[\mathbf{r}, \{\mathbf{R}_n(t)\}]$ as follows [21]:

$$\mathcal{E}^{TB}[\rho] \approx \sum_{k=2}^M (1/k!) \int \Delta\rho(\mathbf{r}_1, t) \cdots \Delta\rho(\mathbf{r}_k, t) F_k(\mathbf{r}_1, \dots, \mathbf{r}_k) \, d\mathbf{r}_1 \cdots d\mathbf{r}_k. \quad (47)$$

Here, $F_k(\mathbf{r}_1, \dots, \mathbf{r}_k) = (\delta^k \mathcal{E}_{hxc} / \delta\rho(\mathbf{r}_1, t) \cdots \delta\rho(\mathbf{r}_k, t))_{\rho=\rho_0}$, and M defines the order of the approximation. $M = 2$ would correspond to the functionals used in references [22] and [23].

Using equation (46), we may write

$$\sum_i \langle \psi_i(t) | \hat{T} | \psi_i(t) \rangle + \mathcal{E}[\rho] = \text{Tr}[\hat{H}^0(\tilde{\Omega} - \tilde{\Omega}_0)] + \mathcal{E}^{TB}[\rho] + \Delta\mathcal{E} + C \quad (48)$$

where

$$\hat{H}^0 = \hat{T} + \hat{V}_0 \quad \hat{V}_0 = \int |\mathbf{r}\rangle V_0(\mathbf{r}, t) \langle \mathbf{r}| \, d\mathbf{r} \quad (49)$$

$$C = \sum_n (T_n + \mathcal{E}_n) \quad (50)$$

$$\Delta\mathcal{E} = \mathcal{E}[\rho_0] - \sum_n \mathcal{E}_n. \quad (51)$$

Here, $\text{Tr}[\zeta|\hat{A}|\zeta] = \langle \zeta | \hat{A} | \zeta \rangle$ for any one-electron state $|\zeta\rangle$, for any operator \hat{A} . $T_n = \text{Tr}[\hat{T}\tilde{\Omega}_n] = \sum_{\gamma} f_{n\gamma} \langle \phi_{n\gamma} | \hat{T} | \phi_{n\gamma} \rangle$ is the kinetic energy of the valence electrons in atom n in isolation, and is a constant. $\mathcal{E}_n = \int \rho_n[\mathbf{r} - \mathbf{R}_n(t)] v_n[\mathbf{r} - \mathbf{R}_n(t)] \, d\mathbf{r} + \mathcal{E}_{hxc}[\rho_n]$ is the electrostatic and exchange–correlation energy of atom n in isolation, and is a constant. C is a sum of electronic energies of free atoms, and is a constant. $\Delta\mathcal{E} = \Delta\mathcal{E}[\{\mathbf{R}_n(t)\}]$ is a function only of the ionic positions. Equation (48) is exact, apart from a possible finite-order approximation to \mathcal{E}^{TB} , as in equation (47). Equation (48) serves as the basis for TD TB.

We now move forward to section 4, and as the basis $\{|\beta\rangle\}$ we select the set of atomic orbitals $\{|\phi_{n\gamma}\rangle\}$. Since $\langle \mathbf{r} | \phi_{n\gamma} \rangle = \phi_{n\gamma}[\mathbf{r} - \mathbf{R}_n(t)]$ is a function only of $[\mathbf{r} - \mathbf{R}_n(t)]$, equations (30) and (33) become $\nabla\phi_{n\gamma}[\mathbf{r} - \mathbf{R}_n(t)] + \nabla_n\phi_{n\gamma}[\mathbf{r} - \mathbf{R}_n(t)] = 0$ and $|\dot{\phi}_{n\gamma}\rangle = |\nabla_n\phi_{n\gamma}\rangle \cdot \dot{\mathbf{R}}_n(t)$, with $|\nabla_n\phi_{n\gamma}\rangle$ defined by $\langle \mathbf{r} | \nabla_n\phi_{n\gamma} \rangle = \nabla_n\langle \mathbf{r} | \phi_{n\gamma} \rangle$. Let us define

$$\mathbf{Q}_{n\gamma n'\gamma'} = \langle \phi_{n\gamma} | \nabla_n \phi_{n'\gamma'} \rangle = -\langle \phi_{n\gamma} | \nabla \phi_{n'\gamma'} \rangle = (1/i\hbar) \langle \phi_{n\gamma} | \hat{p} | \phi_{n'\gamma'} \rangle \quad (52)$$

where $|\nabla\phi_{n'\gamma'}\rangle$ is defined by $\langle \mathbf{r} | \nabla\phi_{n'\gamma'} \rangle = \nabla\langle \mathbf{r} | \phi_{n'\gamma'} \rangle$. Let us introduce the Hermitian matrices

$$H_{n\gamma n'\gamma'}^0 = \langle \phi_{n\gamma} | \hat{H}^0 | \phi_{n'\gamma'} \rangle \quad (53)$$

$$S_{n\gamma n'\gamma'} = \langle \phi_{n\gamma} | \phi_{n'\gamma'} \rangle. \quad (54)$$

Following equations (31) and (32), we write

$$|\psi_i(t)\rangle = \sum_{n,\gamma} \psi_{n\gamma}^i(t) |\phi_{n\gamma}\rangle \quad (55)$$

$$|\dot{\psi}_i(t)\rangle = \sum_{n,\gamma} [\dot{\psi}_{n\gamma}^i(t) |\phi_{n\gamma}\rangle + \psi_{n\gamma}^i(t) |\dot{\phi}_{n\gamma}\rangle]. \quad (56)$$

The valence electron density in equation (43) is given by

$$\rho = \rho(\mathbf{r}, t) = \sum_{i,n,\gamma,n',\gamma'} \psi_{n\gamma}^{i*}(t) \phi_{n\gamma}^*[\mathbf{r} - \mathbf{R}_n(t)] \phi_{n'\gamma'}[\mathbf{r} - \mathbf{R}_{n'}(t)] \psi_{n'\gamma'}^i(t). \quad (57)$$

Finally, let us define the Hermitian TB density matrices:

$$\Omega_{n'\gamma'n\gamma} = \sum_i \psi_{n'\gamma'}^{i*}(t) \psi_{n\gamma}^i(t) \quad (58)$$

$$\Omega_{n'\gamma'n\gamma}^0 = \delta_{nn'} \delta_{\gamma\gamma'} f_{n\gamma}. \quad (59)$$

The Lagrangian in equation (35) now becomes

$$\begin{aligned} L^{TB} &= L^{TB}(\{\psi_{n\gamma}^i\}, \{\dot{\psi}_{n\gamma}^i\}, \{\psi_{n\gamma}^{i*}\}, \{\dot{\psi}_{n\gamma}^{i*}\}, \{\mathbf{R}_n\}, \{\dot{\mathbf{R}}_n\}) \\ &= i\hbar \sum_{n,\gamma,n',\gamma'} \Omega_{n'\gamma'n\gamma} \mathbf{Q}_{n\gamma n'\gamma'} \cdot \dot{\mathbf{R}}_{n'} + i\hbar \sum_{i,n,\gamma,n',\gamma'} \psi_{n\gamma}^{i*} S_{n\gamma n'\gamma'} \dot{\psi}_{n'\gamma'}^i \\ &\quad - \sum_{n,\gamma,n',\gamma'} (\Omega_{n'\gamma'n\gamma} - \Omega_{n'\gamma'n\gamma}^0) H_{n\gamma n'\gamma'}^0 - \mathcal{E}^{TB}[\rho] \\ &\quad + \sum_n M_n \dot{\mathbf{R}}_n^2 / 2 - \phi^{TB}(\{\mathbf{R}_n\}) - C \end{aligned} \quad (60)$$

where $\psi_{n\gamma}^i = \psi_{n\gamma}^i(t)$, $\mathbf{R}_n = \mathbf{R}_n(t)$, ρ is given by equation (57) and

$$\phi^{TB}(\{\mathbf{R}_n\}) = \phi(\{\mathbf{R}_n\}) + \Delta\mathcal{E}(\{\mathbf{R}_n\}). \quad (61)$$

ϕ^{TB} is the total change in electrostatic and exchange–correlation energy as the free atoms are brought together and rigidly superimposed from infinity [2, 24]. ϕ^{TB} involves only properties of free atoms, namely the density ρ_0 in equations (45) and (51) and the original ion–ion interaction potential ϕ . Therefore, ϕ^{TB} is an *a priori* function solely of the atomic species and their positions. ϕ^{TB} can be approximated by a repulsive pair potential [2, 24]. Before deriving the equations of motion from L^{TB} , we now make an aside to extend the derivation to TB models with empirical parameters.

5.2. Empirical tight binding

So far, it has been shown how the quantities appearing in the Lagrangian L^{TB} in equation (60) are to be obtained in a first-principles calculation. However, one may wish to make simplified model assumptions about these quantities. It is therefore desirable to keep the dynamical TB equations open to such empirical models. This is possible, because all derivations, starting from equation (60), require only certain algebraic properties of the quantities $S_{n\gamma n'\gamma'}$, $\mathbf{Q}_{n\gamma n'\gamma'}$, $H_{n\gamma n'\gamma'}^0$, \mathcal{E}^{TB} , ϕ^{TB} and $\Omega_{n'\gamma'n\gamma}^0$. These properties are the following.

(i) The matrix $S_{n\gamma n'\gamma'}$ is Hermitian and invertible. For $n \neq n'$, for given γ and γ' , $S_{n\gamma n'\gamma'}$ depends only on $\mathbf{R}_n - \mathbf{R}_{n'}$, whence $\nabla_n S_{n\gamma n'\gamma'} + \nabla_{n'} S_{n\gamma n'\gamma'} = 0$. $S_{n\gamma n\gamma}$ is independent of \mathbf{R}_n .

(ii) $\mathbf{Q}_{n\gamma n'\gamma'}$ satisfies

$$\mathbf{Q}_{n\gamma n'\gamma'} = \nabla_{n'} S_{n\gamma n'\gamma'} = -\nabla_n S_{n\gamma n'\gamma'} = -\nabla_n S_{n'\gamma' n\gamma}^* = -\mathbf{Q}_{n'\gamma' n\gamma}^* \quad n \neq n' \quad (62)$$

$$\mathbf{Q}_{n\gamma n\gamma} = -\mathbf{Q}_{n'\gamma' n\gamma}^* \quad (63)$$

$\mathbf{Q}_{n\gamma n\gamma}$ is independent of \mathbf{R}_n .

- (iii) The matrix $H_{n\gamma n'\gamma'}^0$ is Hermitian. $H_{n\gamma n'\gamma'}^0$ is a function only of the ionic positions $\{\mathbf{R}_n\}$. $H_{n\gamma n'\gamma'}^0$ is invariant under rigid translations of the ions as a whole, whence $\sum_{n''} \nabla_{n''} H_{n\gamma n'\gamma'}^0 = 0$.
- (iv) $\mathcal{E}^{TB} = \mathcal{E}^{TB}(\{\psi_{n\gamma}^i, \{\psi_{n\gamma}^{i*}, \{\mathbf{R}_n\})$ is such that

$$\partial \mathcal{E}^{TB} / \partial \psi_{n\gamma}^{i*} = \sum_{n', \gamma'} V_{n\gamma n'\gamma'}^{TB} \psi_{n'\gamma'}^i = (\partial \mathcal{E}^{TB} / \partial \psi_{n\gamma}^i)^* \quad (64)$$

where $V_{n\gamma n'\gamma'}^{TB}$ is Hermitian. For given $\{\psi_{i\beta}\}$, \mathcal{E}^{TB} is invariant under the transformation $\{\mathbf{R}_n\} \rightarrow \{\mathbf{R}_n + \Delta\}$, for any Δ . Hence, $\nabla_n \mathcal{E}^{TB} = (\partial \mathcal{E}^{TB} / \partial \mathbf{R}_n)_{\{\psi_{n\gamma}^i, \{\psi_{n\gamma}^{i*}, \{\mathbf{R}_{m \neq n}\}}$ satisfies $\sum_n \nabla_n \mathcal{E}^{TB} = 0$. If we are deriving our TB model from first principles, then, by analogy with equation (23), $V_{n\gamma n'\gamma'}^{TB} = \langle \phi_{n\gamma} | \hat{V}^{TB} | \phi_{n'\gamma'} \rangle$, where $\hat{V}^{TB} = \int |\mathbf{r}\rangle V^{TB}(\mathbf{r}, t) \langle \mathbf{r}| d\mathbf{r}$, $V^{TB}(\mathbf{r}, t) = \delta \mathcal{E}^{TB}[\rho] / \delta \rho$, with ρ given by equation (57).

- (v) ϕ^{TB} is a function only of the ionic positions $\{\mathbf{R}_n\}$. ϕ^{TB} is invariant under rigid translations of the ions as a whole, whence $\sum_n \nabla_n \phi^{TB} = 0$.
- (vi) $\{f_{n\gamma}\}$ in equation (59) are constants. C is an arbitrary constant.

The above properties are satisfied in the first-principles TB set-up in subsection 5.1. All derivations from this point onward rely only on these properties. Therefore, all results below apply not only to first-principles TB but also to any empirical TB model whose parameters satisfy the above properties.

5.3. Lagrangian equations of motion

The Lagrangian equations of motion, corresponding to L^{TB} in equation (60), are given by equations (8), (9) and (10), with L replaced by L^{TB} and with ψ_α and ψ_α^* replaced by $\psi_{n\gamma}^i$ and $\psi_{n\gamma}^{i*}$, respectively. The evaluation of these equations requires only properties (i)–(vi) above. Equation (9) yields the TD SE

$$i\hbar \sum_{n', \gamma'} \mathbf{Q}_{n\gamma n'\gamma'} \cdot \dot{\mathbf{R}}_{n'}(t) \psi_{n'\gamma'}^i(t) + i\hbar \sum_{n', \gamma'} S_{n\gamma n'\gamma'} \dot{\psi}_{n'\gamma'}^i(t) = \sum_{n', \gamma'} H_{n\gamma n'\gamma'}^{TB} \psi_{n'\gamma'}^i(t) \quad (65)$$

where

$$H_{n\gamma n'\gamma'}^{TB} = H_{n\gamma n'\gamma'}^0 + V_{n\gamma n'\gamma'}^{TB} \quad (66)$$

$V_{n\gamma n'\gamma'}^{TB}$ is given by equation (64). $\mathbf{Q}_{n\gamma n'\gamma'}$, $S_{n\gamma n'\gamma'}$ and $H_{n\gamma n'\gamma'}^0$ depend on time via their dependence on the ionic positions $\{\mathbf{R}_n(t)\}$. $V_{n\gamma n'\gamma'}^{TB}$ depends on time via its dependence on $\{\mathbf{R}_n(t)\}$ and on $\{\psi_{n\gamma}^i(t)\}$. Equation (8) gives the complex conjugate of equation (65).

The third Lagrangian equation gives the HF theorem

$$\begin{aligned} M_n \ddot{\mathbf{R}}_n(t) = & - \sum_{n', \gamma', n'', \gamma''} (\Omega_{n''\gamma'' n'\gamma'} - \Omega_{n''\gamma'' n'\gamma'}^0) \nabla_n H_{n'\gamma' n''\gamma''}^0 - \nabla_n \mathcal{E}^{TB} - \nabla_n \phi^{TB} \\ & - \sum_{\gamma, n', \gamma', n'', \gamma'', n''', \gamma'''} (\mathbf{Q}_{n\gamma n'\gamma'} S_{n'\gamma' n''\gamma''}^{-1} H_{n''\gamma'' n'''\gamma'''}^{TB} \Omega_{n'''\gamma''' n\gamma} + \text{c.c.}) \\ & - i\hbar \sum_{\gamma, n', \gamma'} [\Omega_{n'\gamma' n\gamma} \dot{\mathbf{R}}_{n'}(t) \cdot \nabla_{n'} \mathbf{Q}_{n\gamma n'\gamma'} - \text{c.c.}] \\ & + i\hbar \sum_{\gamma, n', \gamma', n'', \gamma'', n''', \gamma'''} \{ \mathbf{Q}_{n\gamma n'\gamma'} S_{n'\gamma' n''\gamma''}^{-1} [\mathbf{Q}_{n''\gamma'' n'''\gamma'''} \cdot \dot{\mathbf{R}}_{n'''}(t)] \Omega_{n'''\gamma''' n\gamma} - \text{c.c.} \} \end{aligned} \quad (67)$$

where $\nabla_n \mathcal{E}^{TB} = (\partial \mathcal{E}^{TB} / \partial \mathbf{R}_n)_{\{\psi_{n\gamma}^i\}, \{\psi_{n\gamma}^{i*}\}, \{\mathbf{R}_m \neq n\}}$. The energy of the system is given by the Legendre transformation

$$\begin{aligned} E^{TB} &= \sum_{i,n,\gamma} \dot{\psi}_{n\gamma}^i (\partial L^{TB} / \partial \dot{\psi}_{n\gamma}^i) + \sum_{i,n,\gamma} \dot{\psi}_{n\gamma}^{i*} (\partial L^{TB} / \partial \dot{\psi}_{n\gamma}^{i*}) + \sum_n \dot{\mathbf{R}}_n \cdot (\partial L^{TB} / \partial \dot{\mathbf{R}}_n) - L^{TB} \\ &= \sum_{n,\gamma,n',\gamma'} (\Omega_{n'\gamma'n\gamma} - \Omega_{n'\gamma'n\gamma}^0) H_{n\gamma n'\gamma'}^0 + \mathcal{E}^{TB}[\{\psi_{n\gamma}^i(t)\}, \{\psi_{n\gamma}^{i*}(t)\}, \{\mathbf{R}_n(t)\}] \\ &\quad + \sum_n M_n [\dot{\mathbf{R}}_n(t)]^2 / 2 + \phi^{TB}[\{\mathbf{R}_n(t)\}] + C. \end{aligned} \quad (68)$$

Subject to a given set of initial conditions, specifying $\{\psi_{n\gamma}^i(t)\}$, $\{\mathbf{R}_n(t)\}$ and $\{\dot{\mathbf{R}}_n(t)\}$ at some time, equations (65) and (67) produce unique values for these variables at any later time. Subject to the provisos in section 2, equations (65) and (67) define a dynamical description of the system of electrons and ions. In this description, the electrons are not confined to an instantaneous stationary state.

5.4. Conserved quantities

It may be verified explicitly that equation (65) conserves the inner product $\sum_{n,\gamma,n',\gamma'} \psi_{n\gamma}^{i*}(t) S_{n\gamma n'\gamma'} \dot{\psi}_{n'\gamma'}^j(t)$. Hence, as before, it is not necessary to impose orthonormality as a separate constraint in the Lagrangian variational procedure. Since L^{TB} has no explicit time dependence, E^{TB} in equation (68) is a constant of the motion [18]. It may be verified explicitly that equations (65) and (67) guarantee $\dot{E}^{TB} = 0$.

For given $\{\psi_{n\gamma}^i\}$ and $\{\psi_{n\gamma}^{i*}\}$, L^{TB} is invariant under the transformation $\{\mathbf{R}_n\} \rightarrow \{\mathbf{R}_n + \Delta\}$, for any Δ . Hence, $\sum_n \partial L^{TB} / \partial \mathbf{R}_n = 0$. Then equation (10) implies that the quantity

$$\mathbf{P} = i\hbar \sum_{n,\gamma,n',\gamma'} \mathbf{Q}_{n\gamma n'\gamma'} \Omega_{n'\gamma'n\gamma} + \sum_n M_n \dot{\mathbf{R}}_n(t) \quad (69)$$

is a constant of the motion. It may be verified explicitly that equations (65) and (67) guarantee $\dot{\mathbf{P}} = 0$. In view of equation (52), in a first-principles TB scheme the quantity $i\hbar \sum_{n,\gamma,n',\gamma'} \mathbf{Q}_{n\gamma n'\gamma'} \Omega_{n'\gamma'n\gamma}$ above may be identified as $\mathbf{P}_e(t)$ in equation (26). Then $\dot{\mathbf{P}} = 0$ is a statement of momentum conservation, in the same sense as equation (42). In an empirical TB model, $S_{n\gamma n'\gamma'}$ and $\mathbf{Q}_{n\gamma n'\gamma'}$ are ‘user-defined’ parameters. In that case, the extent to which the quantity $i\hbar \sum_{n,\gamma,n',\gamma'} \mathbf{Q}_{n\gamma n'\gamma'} \Omega_{n'\gamma'n\gamma}$ may be taken to represent $\mathbf{P}_e(t)$ depends on how physical the assumed form of $S_{n\gamma n'\gamma'}$ is. In all cases, however, \mathbf{P} in equation (69) is a conserved quantity in the theory.

5.5. Stationary states and self-consistency

The stationary states of a quantum system may be obtained as stationary points of the energy of the system subject to the constraint of fixed state norm [25]. To find the stationary states of our system of electrons for a given set of ionic positions $\{\mathbf{R}_n\}$, we imagine that the ions are frozen in these positions, and we consider the energy of the system, given by equation (68). We replace the quantities $\{\psi_{n\gamma}^i(t)\}$ and $\{\psi_{n\gamma}^{i*}(t)\}$ in E^{TB} by a set of variables $\{c_{n\gamma}^i\}$ and $\{c_{n\gamma}^{i*}\}$, respectively, and we seek stationary values of E^{TB} with respect to³ $\{c_{n\gamma}^i\}$ and $\{c_{n\gamma}^{i*}\}$, subject to

³ As in the Lagrangian variational procedure, the real and imaginary parts of $c_{n\gamma}^i$ must be treated as independent variables. This is equivalent to treating $c_{n\gamma}^i$ and $c_{n\gamma}^{i*}$ as independent variables.

the constraint $\sum_{n,\gamma,n',\gamma'} c_{n\gamma}^{i*} S_{n\gamma n'\gamma'} c_{n'\gamma'}^i = 1$. This yields a set of N_e eigenvalue equations⁴

$$\sum_{n',\gamma'} H_{n\gamma n'\gamma'}^{TB} c_{n'\gamma'}^i = \epsilon_i \sum_{n',\gamma'} S_{n\gamma n'\gamma'} c_{n'\gamma'}^i \quad H_{n\gamma n'\gamma'}^{TB} = H_{n\gamma n'\gamma'}^0 + V_{n\gamma n'\gamma'}^{TB}. \quad (70)$$

Here, $V_{n\gamma n'\gamma'}^{TB}$ is given by equation (64), with $\{\psi_{n\gamma}^i\}$ and $\{\psi_{n\gamma}^{i*}\}$ replaced by $\{c_{n\gamma}^i\}$ and $\{c_{n\gamma}^{i*}\}$, respectively. We may wish to consider different sets of N_e one-particle states from the full eigenspectrum of the matrix H^{TB} to be used in the construction of E^{TB} and \mathcal{E}^{TB} in this procedure. This may be done by introducing a set of occupation numbers $\{f_k\}$, such that $\sum_k f_k = N_e$ and $\Omega_{n'\gamma'n\gamma} = \sum_k c_{n'\gamma'}^k f_k c_{n\gamma}^{k*}$, where index k runs over all eigenstates of the matrix H^{TB} . Different choices of $\{f_k\}$ represent various stationary states of the N_e -electron system, for the given set of ionic positions. These states include the ground state and excited states. The solutions to equation (70) for each choice of $\{f_k\}$ are self-consistent, in the sense that they return the same $V_{n\gamma n'\gamma'}^{TB}$ via equation (64) as that which appears equation (70).

Let us consider the difference between the TD electron wavefunctions $\{\psi_{n\gamma}^i(t)\}$ in equation (65) and the stationary wavefunctions $\{c_{n\gamma}^i\}$ in equation (70). As stated above, at any time t , $\{\psi_{n\gamma}^i(t)\}$ are determined by the coupled dynamical equations of the system, equations (65) and (67), subject to a given set of initial conditions, specifying $\{\psi_{n\gamma}^i(t)\}$, $\{\mathbf{R}_n(t)\}$ and $\{\dot{\mathbf{R}}_n(t)\}$ at some earlier time. Thus, $\{\psi_{n\gamma}^i(t)\}$ depend on the evolution of the system, leading up to the instantaneous ionic positions at time t .

By contrast, $\{c_{n\gamma}^i\}$ are determined solely by the given set of ionic positions $\{\mathbf{R}_n\}$ and by the given set of occupation numbers $\{f_k\}$ used to construct the eigenvalue problem in equation (70). We may, therefore, write

$$c_{n\gamma}^i = c_{n\gamma}^i(\{\mathbf{R}_n\}, \{f_k\}). \quad (71)$$

The precise functional dependence of $c_{n\gamma}^i$ on $\{\mathbf{R}_n\}$ and $\{f_k\}$ is determined by the forms of $H_{n\gamma n'\gamma'}^0 = H_{n\gamma n'\gamma'}^0(\{\mathbf{R}_n\})$, $\mathcal{E}^{TB} = \mathcal{E}^{TB}(\{c_{n\gamma}^i\}, \{c_{n\gamma}^{i*}\}, \{\mathbf{R}_n\})$ and $S_{n\gamma n'\gamma'} = S_{n\gamma n'\gamma'}(\mathbf{R}_n - \mathbf{R}_{n'})$.

5.6. Born–Oppenheimer approximation

In our discussion of the dynamics of the system so far, we have not imposed requirements of stationarity on the motion of the electrons or ions. As a limiting case, we now consider the stationary limit, defined by two conditions. The first is that the ionic velocities are sufficiently small to make the velocity-dependent terms in equation (67) negligible. The second is that as the ions move, at any time t , the electron subsystem remains in a particular stationary state, defined by equation (70) for the instantaneous ionic positions $\{\mathbf{R}_n(t)\}$, for a given fixed set of occupation numbers $\{f_k\}$. These assumptions constitute the Born–Oppenheimer approximation.

Thus, in the Born–Oppenheimer approximation, $\{\psi_{n\gamma}^i(t)\}$ are no longer determined by equation (65), but are given by

$$\psi_{n\gamma}^i(t) = c_{n\gamma}^i[\{\mathbf{R}_n(t)\}, \{f_k\}] \quad (72)$$

where $\{c_{n\gamma}^i\}$ are the respective self-consistent stationary wavefunctions, used in the construction of E^{TB} and \mathcal{E}^{TB} in the eigenvalue problem in equation (70), for the given set of occupation numbers $\{f_k\}$, for the set of instantaneous ionic positions $\{\mathbf{R}_n(t)\}$. Ignoring the velocity-dependent terms and using equations (62), (63), (70) and (72), we may now cast equation (67)

⁴ In the absence of degeneracies, the solutions are guaranteed to be orthogonal. If there are sets of degenerate solutions, then orthogonality within each such set must be imposed as a separate constraint.

as

$$\begin{aligned}
M_n \ddot{\mathbf{R}}_n(t) = & - \sum_{n', \gamma', n'', \gamma''} (\Omega_{n'' \gamma'' n' \gamma'} - \Omega_{n'' \gamma'' n' \gamma'}^0) \nabla_n H_{n' \gamma' n'' \gamma''}^0 - \nabla_n \mathcal{E}^{TB} - \nabla_n \phi^{TB} \\
& + \sum_{n', \gamma', n'', \gamma''} \Omega_{n'' \gamma'' n' \gamma'}^\epsilon \nabla_n S_{n' \gamma' n'' \gamma''} \quad \Omega_{n'' \gamma'' n' \gamma'}^\epsilon = \sum_i \psi_{n'' \gamma''}^i(t) \epsilon_i \psi_{n' \gamma'}^{i*}(t)
\end{aligned} \tag{73}$$

with $\nabla_n \mathcal{E}^{TB} = (\partial \mathcal{E}^{TB} / \partial \mathbf{R}_n)_{\{\psi_{n\gamma}^i\}, \{\psi_{n\gamma}^{i*}\}, \{\mathbf{R}_{m \neq n}\}}$.

The Born–Oppenheimer approximation allows the above force expression to be derived from an effective conservative potential as follows. In view of equations (71) and (72), for a given set of occupation numbers $\{f_k\}$, the electron wavefunctions $\{\psi_{n\gamma}^i(t)\}$ in the Born–Oppenheimer approximation are parametric functions of the ionic positions $\{\mathbf{R}_n(t)\}$. Then the quantity

$$\begin{aligned}
\tilde{\phi} = \tilde{\phi}[\{\mathbf{R}_n(t)\}, \{f_k\}] = & \sum_{n, \gamma, n', \gamma'} (\Omega_{n' \gamma' n \gamma} - \Omega_{n' \gamma' n \gamma}^0) H_{n \gamma n' \gamma'}^0 \\
& + \mathcal{E}^{TB}[\{\psi_{n\gamma}^i(t)\}, \{\psi_{n\gamma}^{i*}(t)\}, \{\mathbf{R}_n(t)\}] + \phi^{TB}[\{\mathbf{R}_n(t)\}]
\end{aligned} \tag{74}$$

is also a parametric function of $\{\mathbf{R}_n(t)\}$, for the given $\{f_k\}$. Under an infinitesimal variation in $\{\mathbf{R}_n(t)\}$, using equation (70) and the condition $d \sum_{n, \gamma, n', \gamma'} \psi_{n\gamma}^{i*}(t) S_{n \gamma n' \gamma'} \psi_{n' \gamma'}^i(t) = 0$, we find

$$\begin{aligned}
d\tilde{\phi} = & - \sum_{n, \gamma, n', \gamma'} \Omega_{n' \gamma' n \gamma}^\epsilon dS_{n \gamma n' \gamma'} + \sum_{n, \gamma, n', \gamma'} (\Omega_{n' \gamma' n \gamma} - \Omega_{n' \gamma' n \gamma}^0) dH_{n \gamma n' \gamma'}^0 \\
& + \sum_n (\nabla_n \mathcal{E}^{TB}) \cdot d\mathbf{R}_n(t) + d\phi^{TB}
\end{aligned} \tag{75}$$

where $\nabla_n \mathcal{E}^{TB} = (\partial \mathcal{E}^{TB} / \partial \mathbf{R}_n)_{\{\psi_{n\gamma}^i\}, \{\psi_{n\gamma}^{i*}\}, \{\mathbf{R}_{m \neq n}\}}$. Since both sides of equation (75) involve exact differentials, we may deduce

$$\begin{aligned}
\nabla_n \tilde{\phi} = & \sum_{n', \gamma', n'', \gamma''} (\Omega_{n'' \gamma'' n' \gamma'} - \Omega_{n'' \gamma'' n' \gamma'}^0) \nabla_n H_{n' \gamma' n'' \gamma''}^0 \\
& - \sum_{n', \gamma', n'', \gamma''} \Omega_{n'' \gamma'' n' \gamma'}^\epsilon \nabla_n S_{n' \gamma' n'' \gamma''} + \nabla_n \mathcal{E}^{TB} + \nabla_n \phi^{TB}
\end{aligned} \tag{76}$$

with $\nabla_n \mathcal{E}^{TB} = (\partial \mathcal{E}^{TB} / \partial \mathbf{R}_n)_{\{\psi_{n\gamma}^i\}, \{\psi_{n\gamma}^{i*}\}, \{\mathbf{R}_{m \neq n}\}}$. By conservation of energy, as the system of electron and ions evolves, we must have $\dot{E}^{TB} = \sum_n [\nabla_n \tilde{\phi} + M_n \dot{\mathbf{R}}_n(t)] \cdot \dot{\mathbf{R}}_n(t) = 0$, where $\tilde{\phi} = \tilde{\phi}[\{\mathbf{R}_n(t)\}, \{f_k\}]$. Ignoring, by assumption, any dependence of the ionic accelerations on the ionic velocities, we may now deduce

$$M_n \ddot{\mathbf{R}}_n(t) = -\nabla_n \tilde{\phi} \quad \tilde{\phi} = \tilde{\phi}[\{\mathbf{R}_n(t)\}, \{f_k\}]. \tag{77}$$

This gives the force expression of equation (73) but derived from an effective potential. The existence of this potential relies on the Born–Oppenheimer approximation, which enables us to view the electron states, and hence the electronic energy of the system, as parametric functions of the ionic positions. If one wishes to allow for variation in the occupation numbers $\{f_k\}$, then $\tilde{\phi}$ must be replaced by an appropriate grand potential, as is done for instance in reference [2].

6. Single-orbital orthogonal tight binding

Insight into the dynamical TB equations may be obtained by considering a simplified empirical TB model. This model is obtained by associating a single spherically symmetric orbital with each ionic site, ignoring the overlap of orbitals on different sites, and assuming a simple form for \mathcal{E}^{TB} with second-order Coulomb-like interactions. This model may be viewed as a

TD generalization of the charge-neutral TB bond model in references [2, 26] with an explicit inclusion of second-order interaction terms. It may also be viewed as a TD monopole version of the multipole self-consistent TB model in reference [22]. Single-orbital orthogonal TB has been shown to give a good description of the elastic properties of the noble metals [26]. In the limit of local charge neutrality, it has been used in time-independent simulations of mechanical structure, steady-state electrical conduction and current-induced forces in small wires [2, 3].

6.1. Parameters of the model

A single type of atomic orbital is present in the model. The overlap matrix, $S_{nn'} = \delta_{nn'}$, is diagonal. $\Omega_{nn'}^0 = \delta_{nn'}\Omega_{nn}^0$ where the constant Ω_{nn}^0 is a parameter of the model [2, 26]. Every simplification in $H_{nn'}^0$ is made. H_{nn}^0 is treated as a constant, independent of the ionic positions. For $n \neq n'$, the hopping integral $H_{nn'}^0 = H_{n'n}^0$ is a function only of the distance between ions n and n' , and is a parameter of the model [2, 26]. ϕ^{TB} is approximated by a repulsive pair potential [2, 24, 26]. For $\mathcal{E}^{TB} = \mathcal{E}^{TB}(\{\psi_n^i\}, \{\psi_n^{i*}\}, \{\mathbf{R}_n\})$ we take the model expression

$$\mathcal{E}^{TB} = (1/2) \sum_n U_n \Delta q_n^2 + (1/2) \sum_n \sum_{n' \neq n} f_{nn'} \Delta q_n \Delta q_{n'} \quad \Delta q_n = \Omega_{nn}^0 - \Omega_{nn}^0. \quad (78)$$

Δq_n can be interpreted as the excess number of electrons at site n . U_n is a constant, independent of the ionic positions. The quantity $f_{nn'} = f_{n'n}$ is a function only of the distance between ions n and n' . U_n and $f_{nn'}$ are parameters of the model [22]. \mathcal{E}^{TB} represents a set of second-order Coulomb-like interactions. $V_{nn'}^{TB}$ in equation (64) is diagonal and is given by

$$V_{nn'}^{TB} = \delta_{nn'} \left(U_n \Delta q_n + \sum_{n'' \neq n} f_{nn''} \Delta q_{n''} \right). \quad (79)$$

In this model, variations in the on-site energy $H_{nn}^{TB} = H_{nn}^0 + V_{nn}^{TB}$ arise solely from the interaction energy \mathcal{E}^{TB} , via V_{nn}^{TB} . The quantity $\nabla_n \mathcal{E}^{TB}$, appearing in equation (67), is given by

$$\nabla_n \mathcal{E}^{TB} = (\partial \mathcal{E}^{TB} / \partial \mathbf{R}_n)_{\{\psi_n^i\}, \{\psi_n^{i*}\}, \{\mathbf{R}_{m \neq n}\}} = \sum_{n' \neq n} \Delta q_n \Delta q_{n'} \nabla_n f_{nn'}. \quad (80)$$

Since $S_{nn'}$ is diagonal, $\mathbf{Q}_{nn'}$ in equation (62) vanishes. Physically, the only sensible choice for the diagonal elements of the matrix \mathbf{Q} is $\mathbf{Q}_{nn} = 0$. Then $\mathbf{Q}_{nn'} = 0$, $\forall n, n'$, and so the first term in the right-hand side of equation (69) vanishes, although, as is shown below, $\dot{\mathbf{P}} = 0$ still holds. This is an example of a situation in which the interpretation of that term as the total momentum of the electrons is problematic. Electrons can flow and carry a current even in orthogonal TB models [2], and one would expect them to carry momentum too. The problem arises because of a physical inconsistency in the model: we have assumed some spatial overlap of the atomic orbitals in allowing non-zero hopping integrals, thus enabling the electrons to move, but we have denied this overlap in the overlap matrix. Finding an alternative definition of electron momentum in orthogonal TB is an interesting problem. A possible line of thought in that problem might start from considering the electron crystal momentum in translationally invariant systems [27]. However, this issue will not be pursued here.

6.2. Equations of motion

The TB TD SE, equation (65), becomes

$$i\hbar \dot{\psi}_n^i(t) = \sum_{n'} H_{nn'}^{TB} \psi_{n'}^i(t) \quad H_{nn'}^{TB} = H_{nn'}^0 + V_{nn'}^{TB} \quad (81)$$

with $V_{nn'}^{TB}$ given by equation (79). Equation (67) for the Newtonian force on ion n now reads

$$M_n \ddot{\mathbf{R}}_n(t) = -2 \sum_{n' \neq n} \text{Re}[\Omega_{n'n}] \nabla_n H_{nn'}^0 - \nabla_n \mathcal{E}^{TB} - \nabla_n \phi^{TB} \quad (82)$$

with $\nabla_n \mathcal{E}^{TB} = (\partial \mathcal{E}^{TB} / \partial \mathbf{R}_n)_{\{\psi_n^i, \{\psi_n^{i*}\}, \{\mathbf{R}_{m \neq n}\}}$ given by equation (80). With the imposition of orthogonality, all velocity-dependent terms have disappeared from these equations. $M_n \ddot{\mathbf{R}}_n(t)$ is now a sum of pairwise bond forces. Hence $\sum_n M_n \ddot{\mathbf{R}}_n(t) = 0$, ensuring that \mathbf{P} in equation (69) is a constant of the motion. The total energy of the system is given by

$$\begin{aligned} E^{TB} = & \sum_{n, n'} (\Omega_{n'n} - \Omega_{n'n}^0) H_{nn'}^0 + \mathcal{E}^{TB}[\{\psi_n^i(t)\}, \{\psi_n^{i*}(t)\}, \{\mathbf{R}_n(t)\}] \\ & + \phi^{TB}[\{\mathbf{R}_n(t)\}] + \sum_n M_n [\dot{\mathbf{R}}_n(t)]^2 / 2 + C. \end{aligned} \quad (83)$$

6.3. Self-consistency and Born–Oppenheimer approximation

The results of subsections 5.5 and 5.6 now take the following form. Equation (70) now reads

$$\sum_{n'} H_{nn'}^{TB} c_{n'}^i = \epsilon_i c_n^i \quad H_{nn'}^{TB} = H_{nn'}^0 + V_{nn'}^{TB}. \quad (84)$$

Here, $V_{nn'}^{TB}$ is given by equation (79), with $\Delta q_n = \Omega_{nn} - \Omega_{nn}^0 = (\sum_k f_k |c_n^k|^2) - \Omega_{nn}^0$, where, once again, index k runs over all eigenstates of the matrix H^{TB} . In the Born–Oppenheimer approximation, following equation (72), we write $\psi_n^i(t) = c_n^i[\{\mathbf{R}_n(t)\}, \{f_k\}]$. This enables us to define the effective interionic potential

$$\begin{aligned} \tilde{\phi} = & \tilde{\phi}[\{\mathbf{R}_n(t)\}, \{f_k\}] \\ = & \sum_{n, n'} (\Omega_{nn'} - \Omega_{nn'}^0) H_{nn'}^0 + \mathcal{E}^{TB}[\{\psi_n^i(t)\}, \{\psi_n^{i*}(t)\}, \{\mathbf{R}_n(t)\}] + \phi^{TB}[\{\mathbf{R}_n(t)\}] + C. \end{aligned} \quad (85)$$

The Newtonian forces on the ions may now be expressed as

$$M_n \ddot{\mathbf{R}}_n(t) = -\nabla_n \tilde{\phi} = -2 \sum_{n' \neq n} \text{Re}[\Omega_{n'n}] \nabla_n H_{nn'}^0 - \nabla_n \mathcal{E}^{TB} - \nabla_n \phi^{TB} \quad (86)$$

with $\nabla_n \mathcal{E}^{TB} = (\partial \mathcal{E}^{TB} / \partial \mathbf{R}_n)_{\{\psi_n^i, \{\psi_n^{i*}\}, \{\mathbf{R}_{m \neq n}\}}$ given by equation (80).

6.4. Local charge neutrality

Let us consider the limit of strong electron–electron repulsion, where $\{U_n\}$ and $\{f_{nn'}\}$ become very large. This limit corresponds to making the capacitance of the system very small. In this limit, the system cannot tolerate the accumulation of excess charges. Hence, either in a time-dependent or in a time-independent situation, in this limit the system will behave in such a way as to keep $\{\Delta q_n\}$ in equation (78) close to zero⁵. We will refer to this limit as the limit of local charge neutrality (LCN).

Physically, in this limit the on-site energy shifts $\{V_{nn}^{TB}\}$ in equation (79) should remain finite. Looked at from a numerical point of view, $\Delta q_n \rightarrow 0$ must in general be achievable with

⁵ One may ask, can we not take as the initial state in a time-dependent calculation a situation in which we have transferred electrons from one end of the system to the other, thereby making the initial values of $\{\Delta q_n\}$ non-zero by construction? If we did make $\{\Delta q_n\}$ finite initially, then in the limit of vanishing capacitance we would generate divergent on-site energy shifts $\{V_{nn}^{TB}\}$. If, on the other hand, as the initial state we wish to take a situation in which the system has been biased to a finite potential difference between the ends, then, from the start, $\{\Delta q_n\}$ will have to be vanishingly small.

finite $\{V_{nn'}^{TB}\}$. But if $\{V_{nn'}^{TB}\}$, linear in $\{U_n\}$, $\{f_{nn'}\}$ and linear in $\{\Delta q_n\}$, remain finite, then the quantities \mathcal{E}^{TB} in equation (78) and $\nabla_n \mathcal{E}^{TB}$ in equation (80), which are linear in $\{U_n\}$, $\{f_{nn'}\}$ and quadratic in $\{\Delta q_n\}$, must tend to zero.

Let now $\Omega_{nn'}^{LCN}$ designate the instantaneous TB density matrix $\Omega_{nn'}$ in a general TD problem, solved with some very large $\{U_n\}$ and $\{f_{nn'}\}$. Since, as argued above, throughout the evolution of the system $\nabla_n \mathcal{E}^{TB} \rightarrow 0$, equation (82) becomes

$$M_n \ddot{\mathbf{R}}_n(t) = -2 \sum_{n' \neq n} \text{Re}[\Omega_{n'n}^{LCN}] \nabla_n H_{nn'}^0 - \nabla_n \phi^{TB}. \quad (87)$$

Within a spin degeneracy factor of 2, which may be introduced at will by working with $N_e/2$ doubly populated states and multiplying the $(N_e/2)$ -state density matrix by 2 [2], equation (87) is the same as the force expression in the presence of electrical current flow, obtained in the charge-neutral TB bond model of reference [2]. In that paper, this expression was derived from a steady-state statistical analysis. Here, this force expression is obtained from a dynamical formalism, without assumptions of stationarity.

Since in the LCN limit $(\Delta q_n V_{nn'}^{TB}) \rightarrow 0$, and since $V_{nn'}^{TB}$ is diagonal, we may write $(\Omega_{nn'}^{LCN} - \Omega_{nn'}^0) H_{n'n}^0 = (\Omega_{nn'}^{LCN} - \Omega_{nn'}^0) H_{n'n}^{TB}$, $\forall n, n'$. Since also $\mathcal{E}^{TB} \rightarrow 0$, equation (83) for the energy of the system now can be written as

$$E^{LCN} = \sum_{n,n'} (\Omega_{nn'}^{LCN} - \Omega_{nn'}^0) H_{n'n}^{TB} + \phi^{TB}[\{\mathbf{R}_n(t)\}] + \sum_n M_n [\dot{\mathbf{R}}_n(t)]^2/2 + C. \quad (88)$$

This is the energy expression in the charge-neutral TB bond model of references [2, 26].

Let us finally consider stationary states and the Born–Oppenheimer approximation in the LCN limit. In looking for self-consistent stationary states, we would be solving equation (84) with some very large $\{U_n\}$ and $\{f_{nn'}\}$. Physically, we know that the solution will have $\Delta q_n \rightarrow 0$, $\forall n$. We may then anticipate this result, and, as the condition for self-consistency, take the requirement that $\{c_n^i\}$ satisfy equation (84), with $\{V_{nn'}^{TB}\}$ adjusted such that $\Delta q_n = (\sum_k f_k |c_n^k|^2) - \Omega_{nn}^0 = 0$, $\forall n$. It may be verified that E^{LCN} , with $\{\psi_n^i(t)\}$ replaced by $\{c_n^i\}$, is then stationary under norm-conserving variations in $\{c_n^i\}$. The effective interionic potential in the Born–Oppenheimer approximation, with $\psi_n^i(t) = c_n^i[\{\mathbf{R}_n(t)\}, \{f_k\}]$, becomes

$$\tilde{\phi}^{LCN} = \tilde{\phi}^{LCN}[\{\mathbf{R}_n(t)\}, \{f_k\}] = \sum_{n,n'} (\Omega_{nn'}^{LCN} - \Omega_{nn'}^0) H_{n'n}^{TB} + \phi^{TB}[\{\mathbf{R}_n(t)\}] + C \quad (89)$$

giving the stationary HF theorem

$$M_n \ddot{\mathbf{R}}_n(t) = -\nabla_n \tilde{\phi}^{LCN} = -2 \sum_{n' \neq n} \text{Re}[\Omega_{n'n}^{LCN}] \nabla_n H_{nn'}^0 - \nabla_n \phi^{TB}. \quad (90)$$

7. Summary

The central results of this paper are equations (65) and (67). Subject to the provisos stated in section 2, these equations give a dynamical TB description of the evolution of an interacting system of quantum electrons and classical ions in non-stationary situations. These equations were shown to conserve norm, energy and momentum. The Lagrangian approach yields these dynamical equations and conservation laws naturally, in a single internally consistent calculation. The usefulness of equation (48) is that the resultant formalism spans a range of TB models within a common framework. These models range from *ab initio* models, with parameters derived from first principles as outlined in subsection 5.1, to empirical TB models, such as the single-orbital orthogonal model in section 6. These models, furthermore, span the range from the LCN limit of strong electron–electron repulsions to the limit of non-interacting

electrons. The latter limit is obtained by setting $V_0(\mathbf{r}, t) = \sum_n v_n[\mathbf{r} - \mathbf{R}_n(t)]$, $\mathcal{E}^{TB} = 0$ and $\Delta\mathcal{E}[\{\mathbf{R}_n(t)\}] = \sum_n \sum_{n' \neq n} \int \rho_n[\mathbf{r} - \mathbf{R}_n(t)] v_{n'}[\mathbf{r} - \mathbf{R}_{n'}(t)] d\mathbf{r}$ in equation (48).

Stationary methods have been developed, using both TB [2] and DFT [19, 28], to model electrical conduction and current-induced forces in small conductors under steady-state conditions. The present formalism corroborates the steady-state TB expression for current-induced forces derived in reference [2], and generalizes it beyond the LCN limit. It also opens up the possibility of using TB to model dynamical transport processes, such as the discharge of two initially charged nanoscale metallic clusters, connected by an atomic wire. The TD TB equations of motion allow ions to interact dynamically with the current-carrying electrons in such processes. These equations, furthermore, allow Coulomb interactions and self-consistency to be included explicitly in the calculation, via the quantity \mathcal{E}^{TB} .

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Appendix 1

Equations (1), (2), (3) and (4) are derived below, starting from a fully quantum picture. This derivation is similar in spirit to the wave-packet analysis discussed in reference [8]. We start from N_e quantum electrons and N_z quantum nuclei without any approximations or constraints. We allow the nuclei to be different from each other. This system is described by the Hamiltonian

$$\mathcal{H}_{\text{full}} = \mathcal{H}_e + \mathcal{H}_{ez} + \mathcal{H}_z \quad (\text{A1.1})$$

where

$$\mathcal{H}_e = \sum_{i=1}^{N_e} \hat{\mathbf{p}}_i^2 / 2m_e + W(\{\hat{\mathbf{r}}_i\}) \quad (\text{A1.2})$$

$$\mathcal{H}_{ez} = \sum_{n=1}^{N_z} \int \hat{\rho}(\mathbf{r}) v_n(\mathbf{r} - \hat{\mathbf{R}}_n) d\mathbf{r} \quad \hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N_e} \delta(\mathbf{r} - \hat{\mathbf{r}}_i) \quad (\text{A1.3})$$

$$\mathcal{H}_z = \sum_{n=1}^{N_z} \hat{\mathbf{P}}_n^2 / 2M_n + \phi(\{\hat{\mathbf{R}}_n\}). \quad (\text{A1.4})$$

Here, $\hat{\mathbf{r}}_i = (\hat{r}_{ix}, \hat{r}_{iy}, \hat{r}_{iz})$ and $\hat{\mathbf{p}}_i = (\hat{p}_{ix}, \hat{p}_{iy}, \hat{p}_{iz})$ are electron position and momentum operators, respectively, and $\hat{\mathbf{R}}_n = (\hat{R}_{nx}, \hat{R}_{ny}, \hat{R}_{nz})$ and $\hat{\mathbf{P}}_n = (\hat{P}_{nx}, \hat{P}_{ny}, \hat{P}_{nz})$ are the position and momentum operators, respectively, for nucleus n . They satisfy the commutation relations $[\hat{r}_{i\mu}, \hat{p}_{j\nu}] = i\hbar \delta_{ij} \delta_{\mu\nu}$ and $[\hat{R}_{m\mu}, \hat{P}_{n\nu}] = i\hbar \delta_{mn} \delta_{\mu\nu}$, with all other commutators equal to zero. As in section 2, ϕ is the nucleus–nucleus interaction, W is the electron–electron interaction, v_n is the interaction potential between an electron and nucleus n and $\hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N_e} \delta(\mathbf{r} - \hat{\mathbf{r}}_i)$ is the electron number-density operator.

The system of electrons and nuclei is described by a many-body state-vector $|\Psi(t)\rangle$ satisfying the TD SE

$$\mathcal{H}_{\text{full}}|\Psi(t)\rangle = i\hbar|\dot{\Psi}(t)\rangle. \quad (\text{A1.5})$$

$|\Psi\rangle$ may be assumed to be properly normalized and antisymmetric under exchange of electron labels. Since the nuclei are all different, there are no particular symmetry requirements on $|\Psi(t)\rangle$ under exchange of nuclear labels.

Let $\langle \hat{A} \rangle$ stand for $\langle \Psi(t) | \hat{A} | \Psi(t) \rangle$, for any operator \hat{A} . Let

$$\mathbf{R}_n(t) = \langle \hat{\mathbf{R}}_n \rangle \quad (\text{A1.6})$$

$$\mathbf{P}_n(t) = \langle \hat{\mathbf{P}}_n \rangle. \quad (\text{A1.7})$$

$\mathbf{R}_n(t)$ and $\mathbf{P}_n(t)$ satisfy

$$\dot{\mathbf{R}}_n(t) = (d/dt)\langle \hat{\mathbf{R}}_n \rangle = (1/i\hbar)\langle [\hat{\mathbf{R}}_n, \mathcal{H}_{\text{full}}] \rangle = \langle \hat{\mathbf{P}}_n \rangle / M_n = \mathbf{P}_n(t) / M_n \quad (\text{A1.8})$$

$$\dot{\mathbf{P}}_n(t) = (d/dt)\langle \hat{\mathbf{P}}_n \rangle = (1/i\hbar)\langle [\hat{\mathbf{P}}_n, \mathcal{H}_{\text{full}}] \rangle = - \int \langle \hat{\rho}(\mathbf{r}) \hat{\nabla}_n v_n(\mathbf{r} - \hat{\mathbf{R}}_n) \rangle d\mathbf{r} - \langle \hat{\nabla}_n \phi(\{\hat{\mathbf{R}}_m\}) \rangle \quad (\text{A1.9})$$

where $\hat{\nabla}_n$ represents the symbolic derivative $\partial/\partial \hat{\mathbf{R}}_n$.

The nuclear motion can now be taken to the classical limit as follows. We imagine that $|\Psi(t)\rangle$ is prepared such as to make the spread of each nuclear position

$$\Delta R_n = \sqrt{\langle \hat{\mathbf{R}}_n^2 \rangle - \langle \hat{\mathbf{R}}_n \rangle^2}$$

sufficiently small to enable us to write

$$\langle f(\{\hat{\mathbf{r}}_i\}, \{\hat{\mathbf{R}}_n\}) \rangle \approx \langle f(\{\hat{\mathbf{r}}_i\}, \{\langle \hat{\mathbf{R}}_n \rangle\}) \rangle = \langle f[\{\hat{\mathbf{r}}_i\}, \{\mathbf{R}_n(t)\}] \rangle \quad (\text{A1.10})$$

for any given function of the electron and nuclear position operators. Next, we observe that, for a given typical nuclear kinetic energy T , by making each nucleus sufficiently massive, we can make $P_n = |\langle \hat{\mathbf{P}}_n \rangle| \sim \sqrt{2M_n T}$ as large as we please. Hence, for a given ΔR_n , we can make the relative spread in the nuclear momentum, $\Delta P_n / P_n \sim \hbar / (P_n \Delta R_n)$ as small as is necessary to enable us to write

$$\langle f(\{\hat{\mathbf{P}}_n\}) \rangle \approx f(\{\langle \hat{\mathbf{P}}_n \rangle\}) = f[\{\mathbf{P}_n(t)\}] \quad (\text{A1.11})$$

for any given function of the nuclear momentum operators. Equation (A1.9) now becomes

$$\dot{\mathbf{P}}_n(t) = - \int \rho(\mathbf{r}, t) \nabla_n v_n[\mathbf{r} - \mathbf{R}_n(t)] d\mathbf{r} - \nabla_n \phi[\{\mathbf{R}_m(t)\}] \quad \rho(\mathbf{r}, t) = \langle \hat{\rho}(\mathbf{r}) \rangle. \quad (\text{A1.12})$$

Equations (A1.8) and (A1.12) are the classical equations of motion of nucleus n .

Next, we determine the effective TD SE for the quantum electrons. We assume that, at some initial time t_0 , $|\Psi(t)\rangle$ may be written as

$$|\Psi_0\rangle = |\Psi(t_0)\rangle = |\Psi_{e0}\rangle |\Psi_{z0}\rangle. \quad (\text{A1.13})$$

Here, $|\Psi_{e0}\rangle$ is an arbitrary normalized antisymmetric many-electron state. $|\Psi_{e0}\rangle$ can be thought of as some linear combination of N_e -electron Slater determinants. $|\Psi_{z0}\rangle$ is an arbitrary normalized many-nucleus state, without any symmetry requirements, but with the requirement that it is such as to satisfy equations (A1.10) and (A1.11). If $f = f(\{\hat{\mathbf{R}}_n\}, \{\hat{\mathbf{P}}_n\})$ and $g = g(\{\hat{\mathbf{r}}_i\}, \{\hat{\mathbf{p}}_i\})$ are an arbitrary nuclear operator and an arbitrary electronic operator, respectively, then $|\Psi_0\rangle$ has the property

$$\langle \Psi_0 | f | \Psi_0 \rangle = \langle \Psi_{z0} | f | \Psi_{z0} \rangle \quad (\text{A1.14})$$

$$\langle \Psi_0 | g | \Psi_0 \rangle = \langle \Psi_{e0} | g | \Psi_{e0} \rangle. \quad (\text{A1.15})$$

Consider now some later time $t > t_0$, such that equations (A1.10) and (A1.11) remain valid throughout the interval from t_0 to t . Let us divide this interval into $N \rightarrow \infty$ time steps $\delta t = (t - t_0)/N$. Let $t_s = t_0 + s \delta t$ and let $|\Psi_s\rangle = |\Psi(t_s)\rangle$, with $s = 0, 1, \dots, N$. In this notation, $t_N = t$ and $|\Psi_N\rangle = |\Psi(t)\rangle$.

Let us consider the expectation value of an arbitrary electronic operator, $g = g(\{\hat{r}_i\}, \{\hat{p}_i\})$, in $|\Psi(t)\rangle$. We write

$$\langle \Psi(t) | g | \Psi(t) \rangle = \langle \Psi_N | g | \Psi_N \rangle \approx \langle \Psi_{N-1} | g + (\delta t / i\hbar) [g, \mathcal{H}_{\text{full}}] | \Psi_{N-1} \rangle \quad (\text{A1.16})$$

$$= \langle \Psi_{N-1} | g + (\delta t / i\hbar) [g, \mathcal{H}_e + \mathcal{H}_{\text{ez}}] | \Psi_{N-1} \rangle \quad (\text{A1.17})$$

$$= \langle \Psi_{N-1} | g + (\delta t / i\hbar) [g, \mathcal{H}_e + \tilde{\mathcal{H}}_{\text{ez}}(t_{N-1})] | \Psi_{N-1} \rangle \quad (\text{A1.18})$$

where we have defined

$$\tilde{\mathcal{H}}_{\text{ez}}(\tau) = \sum_{n=1}^{N_z} \int \hat{\rho}(\mathbf{r}) v_n[\mathbf{r} - \mathbf{R}_n(\tau)] d\mathbf{r}. \quad (\text{A1.19})$$

For equation (A1.16), we have used equation (A1.5). For equation (A1.17), we have used the fact the all electron position and momentum operators commute with all nuclear position and momentum operators. For equation (A1.18), we have used equation (A1.10).

The operator inside the expectation value in equation (A1.18) is a new electronic operator. Defining $g_N = g$ and $g_{N-1} = g_N + (\delta t / i\hbar) [g_N, \mathcal{H}_e + \tilde{\mathcal{H}}_{\text{ez}}(t_{N-1})]$, we may write equation (A1.18) as $\langle \Psi_N | g_N | \Psi_N \rangle = \langle \Psi_{N-1} | g_{N-1} | \Psi_{N-1} \rangle$. Iterating the process backwards, we arrive at

$$\langle \Psi(t) | g | \Psi(t) \rangle = \langle \Psi_N | g_N | \Psi_N \rangle = \langle \Psi_0 | g_0 | \Psi_0 \rangle = \langle \Psi_{e0} | g_0 | \Psi_{e0} \rangle \quad (\text{A1.20})$$

where the electronic operator g_0 is obtained from $g_N = g$ by repeated application of the recurrence relation

$$g_{s-1} = g_s + (\delta t / i\hbar) [g_s, \mathcal{H}_e + \tilde{\mathcal{H}}_{\text{ez}}(t_{s-1})]. \quad (\text{A1.21})$$

For the last step in equation (A1.20), we have used equation (A1.15).

Consider now the many-electron state $|\Psi_e(t)\rangle$, satisfying the TD SE

$$\mathcal{H} |\Psi_e(t)\rangle = i\hbar |\dot{\Psi}_e(t)\rangle \quad \mathcal{H} = \mathcal{H}_e + \tilde{\mathcal{H}}_{\text{ez}}(t) \quad (\text{A1.22})$$

with the initial condition $|\Psi_e(t_0)\rangle = |\Psi_{e0}\rangle$. By repeating the above steps, it may be verified that

$$\langle \Psi_e(t) | g | \Psi_e(t) \rangle = \langle \Psi_{e0} | g_0 | \Psi_{e0} \rangle = \langle \Psi(t) | g | \Psi(t) \rangle. \quad (\text{A1.23})$$

Hence, as far as the expectation value of any electronic property is concerned, equation (A1.22) is equivalent to the full SE, equation (A1.5). In equation (A1.12) we may now use $\rho(\mathbf{r}, t) = \langle \Psi_e(t) | \hat{\rho}(\mathbf{r}) | \Psi_e(t) \rangle$. Using equations (A1.10), (A1.11) and (A1.23), we may write the total energy of the system, $E = \langle \Psi(t) | \mathcal{H}_{\text{full}} | \Psi(t) \rangle$, as

$$E = \langle \Psi_e(t) | \mathcal{H} | \Psi_e(t) \rangle + \sum_{n=1}^{N_z} [\mathbf{P}_n(t)]^2 / 2M_n + \phi[\{\mathbf{R}_n(t)\}] \quad (\text{A1.24})$$

Equations (A1.8), (A1.12), (A1.22) and (A1.24) are the same as equations (3), (4), (2) and (1), respectively.

Equations (A1.10) and (A1.11) require $a \gg \Delta R_n \gg \hbar / \sqrt{2M_n T}$, where a is a typical atomic radius and T is a typical nuclear kinetic energy. For a heavy species like Au at room temperature this condition is reasonably satisfied by $\Delta R_n \sim 10^{-11}$ m. ΔR_n increases with time roughly as $\Delta R_n(t) = \Delta R_n(0) \sqrt{1 + (t/\tau)^2}$, where $\tau = 2M_n \Delta R_n^2(0) / \hbar$ [11]. Hence, in the present case, the nuclear positions will retain their initial spread for a characteristic time of $\tau \sim 10^{-12}$ s, or a few thermal vibration periods.

Appendix 2

Below, equation (42) is derived explicitly from equations (36) and (38). Let

$$P_e(t) = \sum_i \langle \psi_i(t) | \hat{p} | \psi_i(t) \rangle = \sum_{i, \beta, \beta'} \psi_{i\beta}^*(t) \langle \beta | \hat{p} | \beta' \rangle \psi_{i\beta'}(t).$$

Then

$$\begin{aligned} \dot{P}_e(t) &= (d/dt) \sum_{i, \beta, \beta'} \psi_{i\beta}^*(t) \langle \beta | \hat{p} | \beta' \rangle \psi_{i\beta'}(t) \\ &= \sum_{i, \beta, \beta'} [\psi_{i\beta}^*(t) \langle \beta | \hat{p} | \beta' \rangle \dot{\psi}_{i\beta'}(t) + \text{c.c.}] + \sum_{i, \beta, \beta'} [\psi_{i\beta}^*(t) \langle \beta | \hat{p} | \dot{\beta}' \rangle \psi_{i\beta'}(t) + \text{c.c.}] \\ &= i\hbar \sum_{i, \beta, \beta'} [\psi_{i\beta}^*(t) \langle \nabla \beta | \beta' \rangle \dot{\psi}_{i\beta'}(t) - \text{c.c.}] + i\hbar \sum_{i, \beta, \beta'} [\psi_{i\beta}^*(t) \langle \nabla \beta | \dot{\beta}' \rangle \psi_{i\beta'}(t) - \text{c.c.}] \end{aligned} \quad (\text{A2.1})$$

where $|\nabla \beta\rangle$ is defined by $\langle \mathbf{r} | \nabla \beta \rangle = \nabla \langle \mathbf{r} | \beta \rangle$. Invoking equation (36) now gives

$$\begin{aligned} \dot{P}_e(t) &= \sum_{i, \beta, \beta', \beta'', \beta'''} [\psi_{i\beta}^*(t) \langle \nabla \beta | \beta' \rangle S_{\beta'\beta''}^{-1} H_{\beta''\beta'''} \psi_{i\beta'''}(t) + \text{c.c.}] \\ &\quad - i\hbar \sum_{i, \beta, \beta', \beta'', \beta'''} [\psi_{i\beta}^*(t) \langle \nabla \beta | \beta' \rangle S_{\beta'\beta''}^{-1} \langle \beta'' | \dot{\beta}''' \rangle \psi_{i\beta'''}(t) - \text{c.c.}] \\ &\quad + i\hbar \sum_{i, \beta, \beta'} [\psi_{i\beta}^*(t) \langle \nabla \beta | \dot{\beta}' \rangle \psi_{i\beta'}(t) - \text{c.c.}] \end{aligned} \quad (\text{A2.2})$$

Let us now consider the quantity $\sum_n M_n \ddot{\mathbf{R}}_n(t)$, with $M_n \ddot{\mathbf{R}}_n(t)$ given by equation (38). The quantities ϕ , $T_{\beta\beta'}$ and—for given $\{\psi_{i\beta}(t)\}$ — \mathcal{E} are invariant under the transformation $\{\mathbf{R}_n(t)\} \rightarrow \{\mathbf{R}_n(t) + \Delta\}$, for any Δ . Hence, $\sum_n \nabla_n \phi = 0$, $\sum_n \nabla_n T_{\beta\beta'} = 0$ and $\sum_n \nabla_n \mathcal{E} = 0$. Furthermore, from equation (30), $|\nabla \beta\rangle = -\sum_n |\nabla_n \beta\rangle$. Hence, $\sum_n M_n \ddot{\mathbf{R}}_n(t) = -\dot{P}_e(t)$. This is equation (42). If the basis $\{|\beta\rangle\}$ is complete, then $\sum_{\beta, \beta'} \langle \mathbf{r} | \beta \rangle S_{\beta\beta'}^{-1} \langle \beta' | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}')$, and terms involving time derivatives of the basis states cancel out both within equation (38) and within equation (A2.2). If the basis is incomplete, then the velocity-dependent terms in the third and fourth lines in equation (38) are needed for equation (42).

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