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1990 J. Phys.: Condens. Matter 2 5161

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Molecular dynamics for chemically bonded systems

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Received 25 January 1990

Abstract. The Car–Parrinello molecular dynamics–density functional scheme derives reliable forces from the energy functional of Kohn and Sham. We describe an alternative approach based on a related energy functional that can be assigned a value for any density, specifically a superposition of site densities moving with the nuclear sites. ‘In–out’ fluctuations of the site densities are described by parameters that are treated as dynamical variables in a Lagrangian formulation. An important feature of the scheme is its adaptability with respect to the method used to solve the electronic structure part of the problem. Explicit calculations for the H₂ molecule illustrate how the scheme can be used with the electrons described in terms of a localised orbital basis.

1. General scheme

Molecular dynamics (MD) simulations have been extremely successful in describing the properties of systems of atoms for which the interatomic forces are of the van der Waals type and can be modelled in terms of pair interactions. Recently, an MD–density functional MD–DF scheme was introduced (Car and Parrinello 1985) that is in principle generally valid and derives forces from the Kohn–Sham (1965) energy functional $E_{KS}[n]$ at (or very close to) self-consistency. Extensive work has established that this functional, with the local-density approximation (LDA) for exchange and correlation, describes energy variations in chemically bonded systems with useful accuracy and the MD–DF scheme has been applied successfully to treat structural and dynamical bulk (amorphous and liquid) and cluster problems (Car and Parrinello 1988, Galli *et al* 1989a, b, Hohl *et al* 1988). As currently constituted, however, the scheme suffers from three interrelated limitations that must be kept in mind. First, the rapidly varying electronic degrees of freedom $\{\psi_i\}$ with small masses μ_i , in conjunction with their large plane-wave expansion, necessitate an MD time step about one order of magnitude smaller than would be necessary in conventional MD calculations with modelled forces. Second, the extensive plane-wave basis needed to describe the electronic wavefunctions with sufficient accuracy is costly in both CPU and memory (the current practical limit seems to be about 100 second- and third-row main group atoms with about 500 electrons, at which point the cubic scaling of the orthonormalisation procedure with basis size dominates the CPU requirement). Third, the pseudopotential–plane-wave approach prohibits treatment of systems where a frozen core is inappropriate and/or localised d- or f-bonding features are important.

In this note, we outline some ideas with regard to a new framework for performing MD calculations in systems with chemical interactions that is more flexible than the original MD–DF scheme and should be simpler to implement where strong potentials are encountered. The new scheme is based on an alternative energy functional $E[n]$ that is stationary at the same density as $E_{\text{KS}}[n]$ but, unlike this functional, can be assigned a value for an arbitrary density, in particular a density constructed by summing spherically symmetric site densities centred on the atoms (Harris 1985, Foulkes and Haydock). Although conceived initially as an approximation to $E_{\text{KS}}[n]$, subsequent work has revealed two important properties of $E[n]$ that greatly enhance its value in connection with electronic structure calculations. The first property, established via explicit calculations, is that the quadratic error made in using $E[n]$ in conjunction with a sum over site densities can be remarkably small to the point of being negligible (Polatoglou and Methfessel 1988, 1990, Finnis 1990). The second property, conjectured by Finnis (1990) on the basis of calculational experience and proved subsequently under weak conditions by Zaremba (1990), is that $E[n]$ is *maximal* at the density n_{sc} , where $E_{\text{KS}}[n]$ is minimal. These two properties imply that maximising $E[n]$ within the range of densities obtainable via a sum of site densities is to all intents and purposes the same as minimising $E_{\text{KS}}[n]$.

To understand why the former procedure is in general easier than the latter it is necessary to write down the two functionals and to discuss how in practice they are evaluated. Although $E_{\text{KS}}[n]$ is a density functional, it can be given a value only for densities n_{out} that belong to the ground state of the one-particle Schrödinger equation with some potential V_{eff} and are constructed from the eigenfunctions of this equation. If the corresponding eigenvalues are denoted ϵ_n , we have

$$E_{\text{KS}}[n_{\text{out}}] = \sum_n a_n \epsilon_n + E_{\text{N}} + \int dx n_{\text{out}}(\mathbf{x}) \left\{ \frac{1}{2} \phi_{\text{out}}(\mathbf{x}) + \epsilon_{\text{xc}}[n_{\text{out}}(\mathbf{x})] + V_{\text{ext}}(\mathbf{x}) - V_{\text{eff}}(\mathbf{x}) \right\} \quad (1)$$

where the a_n are occupation numbers, $\phi_{\text{out}}(\mathbf{x})$ is the Coulomb potential associated with density $n_{\text{out}}(\mathbf{x})$, $\epsilon_{\text{xc}}[n]$ is the LDA exchange–correlation energy density, V_{ext} is the nuclear potential and E_{N} the internuclear repulsion. The functional $E[n]$, on the other hand, can be defined for an arbitrary density $n(\mathbf{x})$ and takes the form

$$E[n] = \sum_n a_n \tilde{\epsilon}_n - \int dx n(\mathbf{x}) \left\{ \frac{1}{2} \phi(\mathbf{x}) + \mu_{\text{xc}}[n(\mathbf{x})] - \epsilon_{\text{xc}}[n(\mathbf{x})] \right\} + E_{\text{N}} \quad (2)$$

where the eigenvalues $\tilde{\epsilon}_n$ are those resulting when the one-particle Schrödinger equation is solved with the potential

$$V_n(\mathbf{x}) = \phi(\mathbf{x}) + \mu_{\text{xc}}[n(\mathbf{x})] + V_{\text{ext}}(\mathbf{x}) \quad (3)$$

the Coulomb potential $\phi(\mathbf{x})$ is that corresponding to $n(\mathbf{x})$ and $\mu_{\text{xc}}[n(\mathbf{x})]$ is the LDA exchange–correlation potential. To evaluate $E[n]$ for given $n(\mathbf{x})$, it is necessary only to calculate the eigenvalues for a specific one-particle potential. The eigenvectors do not appear explicitly in the energy expression and, in particular, the Coulomb potential corresponding to these eigenvectors need not be calculated. This is computationally of some importance if the one-particle equation is solved using a localised or partially localised basis.

To perform an electronic structure calculation using equation (1), one begins with a potential, solves the Schrödinger equation to obtain the density n_{out} evaluates the corresponding Coulomb and exchange–correlation potentials and cycles to self-consistency using the Kohn–Sham self-consistency condition that is satisfied at the minimum of the functional. An alternative self-consistency procedure, most advantageous within the framework of pseudopotential–plane-wave calculations, is iterative minimisation (‘propagation in imaginary time’) with the constraint of orthonormality on the one-particle eigenfunctions ψ_n :

$$\psi_n(\mathbf{r}, t) = -\delta E_{\text{KS}}/\delta \psi_n^*(\mathbf{r}, t) + \text{constraints} = -H\psi_n(\mathbf{r}, t) + \text{constraints} \quad (4)$$

which allows FFT methods to be exploited to their fullest extent (Štich *et al* 1989). In this especially favourable framework, the solution of Poisson’s equation for the density n_{out} is straightforward. Where a plane-wave basis is inappropriate, however, this step is computationally awkward and CPU intensive.

An alternative procedure using equation (2) and making use of the properties of this functional mentioned above is to work with trial densities characterised by parameters D_i . The simplest and probably most appropriate prescription for constructing a trial density is that of Finnis, who superposed neutral atom densities with each site density multiplied by a function that allows ‘in–out’ variation. Finnis used a Fermi function with two parameters per site. While we shall assume throughout this paper that one parameter only per site is sufficient, this is in no sense a restriction and as much variational freedom can be built in as is commensurate with the problem at hand (e.g. for some applications it may be necessary to include on-site polarisation functions that describe site-localised deviations from spherical symmetry.) Starting with a guess for the parameters D_i , the potential in equation (3) is constructed, the Schrödinger equation solved and the function $E[\{D_i\}]$ evaluated. The derivative of $E[\{D_i\}]$ with respect to each D_i is

$$\frac{\partial E[\{D_i\}]}{\partial D_i} = \int d\mathbf{x} [n_{\text{out}}(\mathbf{x}) - n_{\{D_i\}}(\mathbf{x})] \frac{\partial V_{\{D_i\}}(\mathbf{x})}{\partial D_i} \quad (5)$$

where $n_{\text{out}}(\mathbf{x})$ is the density generated by the solution of the Schrödinger equation with potential $V_{\{D_i\}}(\mathbf{x})$, given in terms of the trial density by equation (3). With the aid of these forces, the maximum of $E[\{D_i\}]$ can be found readily using, for example, conjugate gradient methods.

Since the trial density has restricted freedom this procedure will not generate the exact minimum of $E_{\text{KS}}[n]$. However, explicit calculations for aluminium films (Finnis 1990) and for bulk silicon and carbon (Polatoglou and Methfessel 1988, 1990) showed that a limited variation in the site densities was sufficient to give a negligible error (even though the deviations of the trial density from the self-consistent density were in no sense negligible). We expect this to be true in general, and note that the magnitude of the likely error in a specific application can be determined via control calculations with increased variational freedom. As mentioned above, the evaluation of the energy $E[\{D_i\}]$ as well the forces in equation (5) does *not* require the solution of Poisson’s equation for the density $n_{\text{out}}(\mathbf{x})$. The Coulomb potential corresponding to $n_{\{D_i\}}(\mathbf{x})$ is needed, but this is trivially evaluated as a sum over sites because the relation between n and ϕ is linear. This is not true of the exchange–correlation potential, but this is local so that all contributions to the forces in equation (5) involve only single space integrals with well localised integrands.

MD calculations can be performed with the aid of the functional $E[\{D_i\}]$ by treating the site-density parameters as dynamical variables with which are associated small *negative* masses $-M_{D_i}$. The appropriate Lagrangian is then

$$\mathcal{L}[\{\dot{\mathbf{R}}_i\}, \{\dot{D}_i\}, \{D_i\}, \{\dot{D}_i\}] = \frac{1}{2} \sum_i [M_i \dot{\mathbf{R}}_i^2 - M_{D_i} \dot{D}_i^2] - E[\{\dot{\mathbf{R}}_i\}, \{D_i\}]. \quad (6)$$

and the corresponding equations of motion are

$$M_i \ddot{\mathbf{R}}_i = -\nabla_{\mathbf{R}_i} E \quad M_{D_i} \ddot{D}_i = \partial E / \partial D_i. \quad (7)$$

For small mass ratios M_{D_i}/M_i , the forces on the D_i will act so as to drive them continuously towards the *maximum* of E . If a simulation is started with optimal (or 'adiabatic') D_i -values, corresponding to the maximum of $E[\{D_i\}]$ for the corresponding nuclear coordinates, the $D_i(t)$ will tend to oscillate on a short time scale about their local adiabatic values. For suitably chosen masses, the oscillations and the kinetic energy of the D_i motion can be kept small over periods long compared with typical MD-averaging times so that the forces acting on the nuclei will be at all times close to those that would obtain if the energy functional were maximised (approximately equivalent to the Kohn–Sham functional being minimised) in each time step ('adiabatic' dynamics).

Propagation using equation (7) requires calculation of the forces on the nuclei for fixed values of the D_i . On differentiating equation (2) with respect to nuclear coordinate \mathbf{R}_i , one can express these forces as the sum of three terms,

$$-\nabla_{\mathbf{R}_i} E[\{\mathbf{R}_i\}, \{D_i\}] = -\nabla_{\mathbf{R}_i} \Phi_{\{D_i\}}(\mathbf{R}_i) + \int d\mathbf{x} [n_{\{D_i\}}(\mathbf{x}) - n_{\text{out}}(\mathbf{x})] \nabla_{\mathbf{R}_i} V_{\{D_i\}}(\mathbf{x}) + \mathbf{F}_{\text{basis}}. \quad (8)$$

Here $\Phi_{\{D_i\}}(\mathbf{R}_i)$ is the net electrostatic potential at \mathbf{R}_i due to the ions and the trial density $n_{\{D_i\}}(\mathbf{x})$; so the first term in equation (8) gives a Hellman–Feynman-like force on nucleus i . Note that this is to be evaluated *with the trial density*, and not with the output density n_{out} , and is simply a sum of repulsive pair interactions involving the net electrostatic potentials corresponding to the site densities. Thus the Hellman–Feynman contribution to the forces involves, at worst, one-dimensional integrals and a sum over a limited number of neighbours. The second term in equation (8) requires in general three-dimensional integrals over a region localised about site i with integrand proportional to the difference between the trial density $n_{\{D_i\}}(\mathbf{x})$ and the density $n_{\text{out}}(\mathbf{x})$ that results from the solution of the Schrödinger equation. The third term $\mathbf{F}_{\text{basis}}$ gives the so-called 'Pulay-forces' which devolve from any explicit dependence on the nuclear coordinates that the basis used to solve this equation may have. If the basis has no such dependence (as is the case for plane waves in a box), this term is zero. If the trial density happens to coincide with the self-consistent density n_{sc} , then n_{out} does also, the second term in equation (8) is zero and one is left with the usual Hellman–Feynman theorem for the forces. As is well known, this result is useful only when the self-consistent density, including all effects due to core polarisation, is determined very accurately, which in practice is hardly ever the case. The force formula in equation (8), however, includes explicitly all deviations of the trial density from the self-consistent density and is merely the formal gradient of the energy expression, equation (2), provided only that the density n_{out} is expressed in terms of the basis functions used to solve the Schrödinger equation so that basis errors in energy and force are the same. The force formula is modified only trivially if a frozen core is used, or the ion cores are represented by pseudopotentials.

2. Application to the H₂ molecule

We now demonstrate how the ideas outlined above work out in practice via explicit calculations treating the vibration of the protons in an H₂ molecule. Although this is an essentially trivial application having only illustrative value, the system does have a singular potential, which in the present calculation did not have to be replaced by a pseudopotential (Buda *et al* 1989). When a localised basis is used, the computations required to determine the proton dynamics can be performed on a personal computer. As a family of trial site densities we choose exponentials with exponent $D_1 = D_2 = \lambda$ as the dynamical variable discussed above (equations (5)–(8)):

$$n_\lambda(\mathbf{x}) = \frac{\lambda^3}{8\pi} \sum_{i=1,2} \exp(-\lambda|\mathbf{x} - \mathbf{R}_i|). \quad (9)$$

To determine the eigenvalue we use the usual variable-exponent LCAO form for the H₂ 1 σ_g orbital:

$$|\alpha\rangle = \sqrt{\frac{\alpha^3}{2\pi(1+S)}} [\exp(-\alpha|\mathbf{x} - \mathbf{R}_1|) + \exp(-\alpha|\mathbf{x} - \mathbf{R}_2|)] \quad (10)$$

where S is the overlap integral. The energy expression, equation (2), then takes the form

$$E[d, \lambda] = 2 \min_\alpha (\langle \alpha | \hat{T} + V_\lambda | \alpha \rangle - \int d\mathbf{x} n_\lambda(\mathbf{x}) \{ \frac{1}{2} \phi_\lambda(\mathbf{x}) + \mu_{xc}[n_\lambda(\mathbf{x})] - \epsilon_{xc}[n_\lambda(\mathbf{x})] \}) + \frac{1}{d} \quad (11)$$

where $d = |\mathbf{R}_1 - \mathbf{R}_2|$ is the interproton separation. The best estimate of the adiabatic energy obtainable within the restriction of the density variation and orbital basis is then

$$E_{gs}(d) = \max_\lambda (E[d, \lambda]). \quad (12)$$

This is shown in figure 1(a) and is extremely close to the correct Kohn–Sham–LDA H₂ binding energy curve (Gunnarsson and Johansson 1976). The energy zero in figure 1(a) refers to a calculation with a proton separation d of 10 au and with a spin correction included to take account of the energy lowering in the spin-uncompensated atomic state. The corresponding value of 4.78 eV for the well depth is very close to the experimental value of 4.74 eV. The parametrisation given by Vosko *et al* (1980) was used for the exchange–correlation energy and potential and its dependence on the spin polarisation. In the molecular ground-state configuration, the spin polarisation is of course zero. Figure 1(b) shows the variation in $E[d, \lambda]$ with respect to λ for $d = 1.44$ au and illustrates the maximum principle obeyed by the functional in equation (11). The arrows on the energy curves give the gradients of the energy as determined by the force formulae, equations (8) and (5) for figures 1(a) and 1(b) respectively and illustrate that these formulae do give the correct derivatives of the energy functional, including the basis error. The forces in figure 1(a) include explicitly the ‘Pulay’ or ‘basis’ terms, which

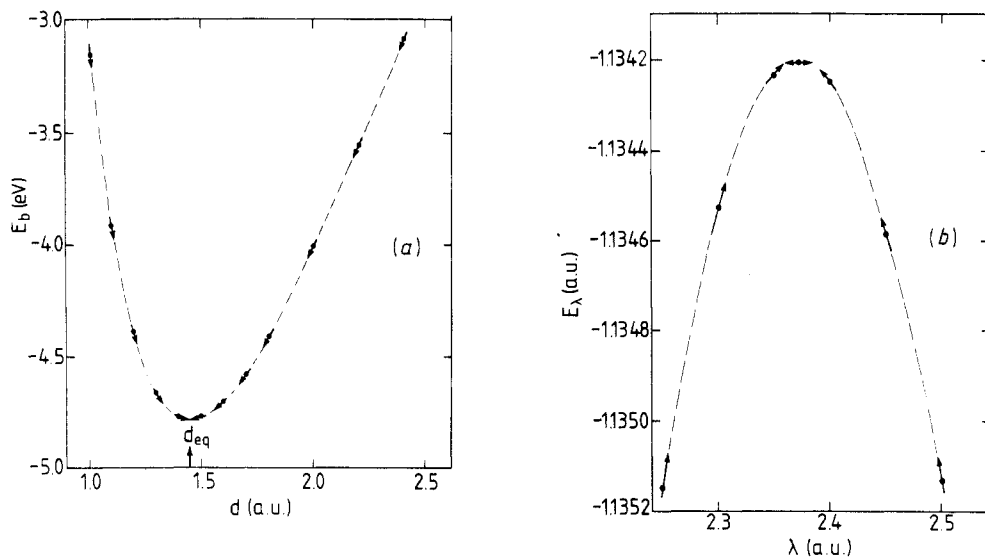


Figure 1. (a) Binding energy curve of H_2 as given by equation (11). The arrows denote the gradient of the energy curve as determined by the force formula, equation (8). (b) Dependence of $E[d, \lambda]$ on λ for $d = 1.44$ au. The arrows denote the gradient as determined by the force formula, equation (5).

are of the same order of magnitude as the other terms and are therefore vital to a proper force calculation.

The adiabatic motion of the protons can be described in a number of ways. The most direct is to perform the maximisation in equation (12) to determine the energy and forces in each MD time step. This is of course straightforward in the present case but inefficient in general when the maximisation involves many parameters rather than one. By treating the parameter λ as a dynamical variable in a Lagrangian of the form of equation (6) with an appropriate mass, the maximisation step can be eliminated. Figure 2(a) shows results of a dynamical simulation performed using the equations of motion (7), with masses $M_d = M_p/2$, where M_p is the physical proton mass, and $M_\lambda = 0.001M_d$, for the relative vibrational coordinate d and the density parameter λ , respectively. The trajectory was propagated using the standard Verlet algorithm with a time step $\Delta t = 5.0$ au, about 0.015 times the vibrational period and corresponding to a change in d of about 0.04 au per time step when the protons are travelling at maximum velocity. The simulation was started with the nuclei at rest and separated by 2.0 au, so that the potential energy was 0.77 eV with respect to the well minimum, and the λ coordinate set equal to its adiabatic value (2.17 au) for which the energy, equation (11), at a separation of $d = 2.0$ au is maximal. Figure 2(a) shows the nuclear kinetic energy T (in eV), the internuclear separation d and the value of the density parameter λ (in au) as a function of time for the subsequent motion through two vibrational periods. The variation in λ was found to correspond very closely to adiabaticity (i.e. $\lambda(t) \simeq \lambda_{\max}[d(t)]$, where $\lambda_{\max}[d]$ maximises the energy in equation (11) for proton separation d) so that the forces acting on the protons were at all times very close to the derivative of the ground-state energy curve in figure 1(a). The kinetic energy associated with the λ -coordinate oscillated within the range from -0.15 to 0 meV, compared with the maximum value of the nuclear kinetic energy of 0.77 eV. The simulation was

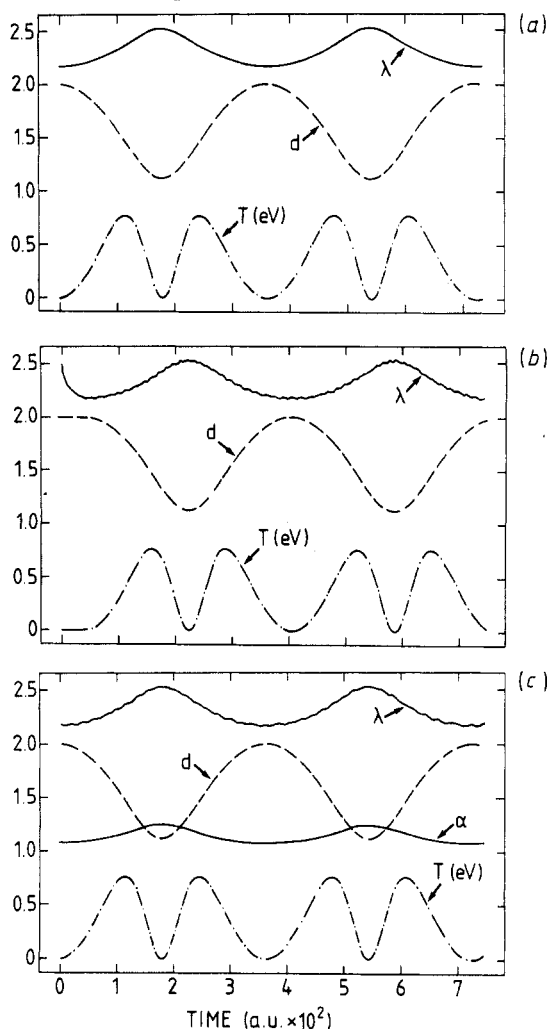


Figure 2. Simulation of the oscillation of the two protons in an H_2 molecule as given by the classical equations of motion, equation (6). The simulations were started at $d = 2.0$ au and run for two vibrational periods. The lowest curve gives the kinetic energy T of the protons. The upper curves give the values of $d(t)$ and $\lambda(t)$ (au) in (a) and (b) and $\alpha(t)$, $d(t)$ and $\lambda(t)$ in (c). In (a) and (b) only λ was treated dynamically with the minimisation with respect to α (equation (11)) carried out explicitly in each time step. In (c), both λ and α were treated dynamically using the potential function, equation (13). The time step was 5.0 au. The simulations in (a) and (c) were started adiabatically and remained very close to adiabatic throughout. The simulation in (b) was started with λ far from its adiabatic value and adiabaticity was established via an initial quench.

continued for a total of ten vibrational periods during which each atom moved by about 9 au with no detectable drift in the kinetic energy of the λ -subsystem. This indicates that with the given choice of relative mass M_λ/M_d , heating of the λ -subsystem was minimal so that 'quenches' of λ to the electronic ground state will be necessary only after periods of time comparable with or longer than typical MD averaging times. Near-adiabatic dynamics was found for values of M_λ/M_d in the range 0.001–0.05 and will occur in general provided that the mass ratio and the coupling are small and the

'natural frequencies' of the auxiliary variables ω_{D_i} (e.g. ω_λ is governed by M_λ and the force constant (about 0.13 au) characterising the energy variation shown in figure 1(b)) are much larger than those of the nuclear motion. For linearly coupled oscillators with frequencies ω_λ, ω_d , for example, the non-adiabaticity of the low-frequency oscillation (ω_d) is determined to lowest order in the coupling by the parameter

$$P = (M_\lambda/M_d)[\omega_\lambda^2\omega_d^2/(\omega_\lambda^2 - \omega_d^2)^2][\partial\lambda_{\max}(d)/\partial d]^2. \quad (13)$$

This parameter can, of course, be made arbitrarily small by decreasing M_λ , but only at the expense of introducing high-frequency motion in the trajectory, which, although it has only a small amplitude, must be integrated correctly. In practice, therefore, it is most efficient to choose as large a mass as is commensurate with the required level of adiabaticity. The range quoted above for M_λ corresponds to $1.5 \text{ eV} < \omega_\lambda < 10 \text{ eV}$ compared with $\omega_d \approx 0.5 \text{ eV}$.

Figure 2(b) shows the results of a simulation where initial adiabaticity was established dynamically by starting with small Δt and quenching until the λ -coordinate settles down and its kinetic energy stabilises at a small value ('simulated annealing'). The initial value of λ was in this case 2.5 au, the adiabatic value for separation $d = 1.1$ au and at the extreme of the range encountered in the simulation. As can be seen, a rapid quench established near adiabaticity and the subsequent motion was close to adiabatic, although the λ -coordinate displayed a weak tendency to overshoot. However, the kinetic energy of the λ -coordinate was again extremely small and the nuclear motion was virtually indistinguishable from that in figure 2(a). It was found important to perform a rather thorough quench and attempts to increase the time step with the system too far from adiabaticity resulted in instability. In general, one would expect an initial non-dynamic determination of starting values, to be preferable. The feasibility of such an approach depends on the local structure of E in the $\{D_i\}$ subspace and the possible existence of local maxima with comparable weight.

In the simulations shown in figures 2(a) and (b), the eigenvalue problem was solved extrinsically to the dynamics by performing the minimisation of the expectation value in equation (11) with respect to the orbital exponent α explicitly in each time step. The 'flair' of the MD-DF scheme is that this minimisation is effectively incorporated in the dynamics. Within the present approach, a fully dynamical treatment of the problem — the equivalent of the MD-DF scheme with a localised basis — can be carried out by treating the orbital exponent in equation (10) as a dynamical variable analogous to λ . This can be assigned a positive mass and the propagation carried out with an appropriately extended Lagrangian having a potential energy function

$$E[\alpha, d, \lambda] = 2\langle \alpha | \hat{T} + V_\lambda | \alpha \rangle - \int dx n_\lambda(x) \left\{ \frac{1}{2} \phi_\lambda(x) + \mu_{xc}[n_\lambda(x)] - \epsilon_{xc}[n_\lambda(x)] \right\} + \frac{1}{d} \quad (14)$$

and an additional kinetic energy term. Figure 2(c) shows the results of a simulation carried out in this fashion with both α and λ set initially at their adiabatic values. As can be seen, the nuclear motion is virtually indistinguishable from that of figures 2(a) and 2(b), demonstrating that, for the H_2 problem at least, the entire electronic structure part of the calculation can be dealt with dynamically with no reduction in the time step. Where feasible, this approach is clearly the most efficient because it requires just a single force calculation per MD time step (as against the two or three necessary to perform an α -minimisation). However, the adiabaticity achieved in figure 2(c), although

entirely adequate, was an order of magnitude worse than in figure 2(a) because the force constants governing the α -motion are large and a relatively large mass M_α was needed in conjunction with the time step Δt of 5 au. The mass parameters used in the simulation shown in figure 2(c) were $M_\alpha = 0.05M_d$ and $M_\lambda = 0.001M_d$, corresponding to $\omega_\alpha, \omega_\lambda \simeq 5$ and 10 eV, respectively. The kinetic energy of the α - λ -system displayed oscillations on a time scale of about $\omega_\alpha^{-1}, \omega_\lambda^{-1}$ superimposed on an envelope oscillation between zero (when the protons approached a turning point) and some maximum value T_{\max} (when the protons were moving most rapidly). For the time span shown in figure 2(c), T_{\max} was about 2 meV. However, as the simulation was allowed to proceed, T_{\max} increased approximately linearly with each oscillation and was about 6 meV (about 1% of the nuclear kinetic energy) after ten round trips, at which point a stabilisation of the trajectory (via re-optimisation or quench) became desirable. This drift could be due to interference between the α - and λ -oscillations and was not present when masses $M_\alpha = 0.02M_d$ and $M_\lambda = 0.015M_d$, corresponding to better separated natural frequencies $\omega_\alpha, \omega_\lambda \simeq 8.2$ and 2.6 eV, were used. With this parameter choice, the 'minimisation' of $E[\alpha, d, \lambda]$ with respect to α occurs on a substantially shorter time scale than the maximisation with respect to λ ; so the propagation conditions approach more closely those in the λ -only simulations using the energy function in equation (11). With a time step Δt of 5 au this simulation gave $T_{\max} \simeq 3.0$ meV (and an average kinetic energy for the α - λ system of about 0.5 meV) and showed no sign of instability or drift over 10 cycles. This behaviour occurs only over a rather limited range of mass parameters, however, which suggests that, in applications with many dynamical variables some of which influence the energy strongly, it may prove difficult to find a tuning of the corresponding mass parameters that allows propagation over long periods of time with a large time step. A second limitation that must be borne in mind in connection with a fully dynamical treatment of systems with more than one electron level is the need to impose the Pauli principle via additional constraints.

Because of these limitations, and depending on the system under study, it may be preferable to calculate the eigenvalue sum explicitly using standard methods and to restrict the dynamical degrees of freedom to the density variables, as in equation (6). In all applications to date, the dependence of the energy on these variables has been found to be quite weak; so one would expect in general that small masses and large time steps can be used. In essence, this procedure amounts to decoupling eigenvalue determination and 'self-consistency' from each other, with the latter part of the problem dealt with dynamically. The former part amounts only to the solution of an eigenvalue problem for a fixed potential. This decoupling introduces considerable flexibility and at least one of the snags encountered when formulating the MD-DF scheme in a localised basis (Gillan and Madden 1988), namely the need to solve Poisson's equation for the 'output' density of the electronic structure calculation, is eliminated. This density is needed only to perform the single space integrals that determine the energy and the forces. Clearly, however, the CPU requirement of the scheme will in general be dominated by the method employed to solve the eigenvalue problem with adequate accuracy. We are currently exploring ways of applying the scheme to a large system and shall report on the results in a future publication.

Acknowledgments

We thank Mike Finnis, Michael Methfessel and Eugene Zaremba for communication of results prior to publication.

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