Introduction to the quantum trajectory method and to Fermi molecular dynamics

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Abstract

The quantum trajectory method (QTM) will be introduced, and an approximation to the QTM known as Fermi molecular dynamics (FMD) will be described. Results of simulations based on FMD will be mentioned for specific nonequilibrium systems dominated by Coulomb interactions.

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For a single particle moving under the influence of a time-dependent potential $U(\vec{r}, t)$, the time-dependent Schrödinger equation (TDSE) may be written as (with $\hbar = 1$, and $m = 1$)

$$i\partial\Psi(\vec{r}, t)/\partial t = \left[-\tfrac{1}{2}\nabla^2 + U(\vec{r}, t)\right]\Psi(\vec{r}, t). \tag{1}$$

This equation can be solved by a variety of well-developed numerical techniques; e.g., upon writing the wavefunction as a sum of its real and imaginary parts

$$\Psi(\vec{r}, t) \equiv \psi_R(\vec{r}, t) + i\psi_I(\vec{r}, t) \tag{2}$$

equation (1) becomes

$$\partial\psi_R(\vec{r}, t)/\partial t = \left[-\tfrac{1}{2}\nabla^2 + U(\vec{r}, t)\right]\psi_I(\vec{r}, t) \tag{3}$$

$$\partial\psi_I(\vec{r}, t)/\partial t = \left[+\tfrac{1}{2}\nabla^2 - U(\vec{r}, t)\right]\psi_R(\vec{r}, t). \tag{4}$$

This coupled pair of partial differential equations can then be solved on a fixed spatial grid of points, using a predictor–corrector or a Bulirsch–Stoer method [1], i.e. as an alternative to the well-known Crank–Nicholson algorithm.

Such a finite-difference approach to the solution of a partial differential equation is equivalent to the solution of a set of $2N$ coupled ordinary differential equations, where N is the number of grid points on which the wavefunction is defined. In three dimensions, these 'grid points' could consist of an expansion of the wavefunction in spherical harmonics, along with a discretization of the radial coordinate. In this formulation, the dependent variables are the values of the real and imaginary parts of the wavefunction at each grid point, labelled by

ℓ, m and k, where $r_k = k\Delta r$, and Δr is the size of the radial step; see [1] for a more complete description.

Then, after making the replacements, $\psi_R(\vec{r}, t) = \phi_R(\vec{r}, t)/r$, and $\psi_I(\vec{r}, t) = \phi_I(\vec{r}, t)/r$, the numerical solution of these equations is straightforward. Not only are the $2N$ equations linear in the real and imaginary parts of the wavefunction, but the wavefunction itself is usually a fairly smooth function of the spatial coordinates and the time; e.g., both $\phi_R \to 0$ and $\phi_I \to 0$, as $r \to 0$, even for particles moving in Coulomb potentials. (Generally, it may be expected that linearity and smooth behaviour are not two completely independent characteristics of these equations.)

It is important to note that for three-dimensional problems, N can easily attain values of 10 000 or more, even for a single particle moving in an external field. Consequently, for two mutually interacting quantum particles, each with a full range of motion, this method is computationally very demanding. For three or more mutually interacting quantum particles, each with a full range of motion, the method is, as of this writing, still quite impractical.

An alternate formulation of this problem is due to Madelung [2] and Bohm [3]. Writing the wavefunction of equation (2) as

$$\Psi(\vec{r}, t) = \exp(C(\vec{r}, t) + iS(\vec{r}, t)) \tag{5}$$

where C and S are both purely real functions of the spatial coordinates and the time, one arrives at the following pair of coupled partial differential equations:

$$\partial C/\partial t = -\nabla C \cdot \nabla S - \tfrac{1}{2}\nabla^2 S \tag{6}$$

$$\partial S/\partial t = -\tfrac{1}{2}|\nabla S|^2 + \tfrac{1}{2}(|\nabla C|^2 + \nabla^2 C) - U. \tag{7}$$

Then, with definitions of the 'quantum potential', Q,

$$Q \equiv -\tfrac{1}{2}(|\nabla C|^2 + \nabla^2 C) \tag{8}$$

and the 'velocity', $\vec{v}$,

$$\vec{v}(\vec{r}, t) \equiv \nabla S \tag{9}$$

equations (6) and (7) become

$$\partial C/\partial t = -\vec{v} \cdot \nabla C - \tfrac{1}{2}\nabla \cdot \vec{v} \tag{10}$$

$$\partial S/\partial t = -\tfrac{1}{2}v^2 - (Q + U). \tag{11}$$

Upon taking the gradient of both sides of equation (11), one also has an equation for the velocity:

$$\partial \vec{v}/\partial t = -\vec{v} \cdot \nabla \vec{v} - \nabla(Q + U). \tag{12}$$

Now, as for the conventionally written TDSE, one can formulate an approach to the numerical solution of equations (10) and (11), or equations (10) and (12), by first defining the dependent variables C and S, or C and $\vec{v}$, on a fixed grid of points. As before, in this way, a pair of coupled partial differential equations is transformed into an equivalent set of coupled ordinary differential equations. However, one suspects that the solution of these equations might not now be so straightforward since the equations are nonlinear.

And, indeed, this is usually found to be the case. Even though C is often found to be reasonably well behaved, Q is usually not well behaved. Small amplitude, rapid spatial variations in C are amplified into large amplitude, rapid spatial variations in Q. These, in turn, appear as large amplitude, rapid spatial variations in both S and $\vec{v}$.

In an attempt to remove some of the nonlinearity from these equations, one may allow next for the fact that, in a moving or Lagrangian coordinate system,

$$\mathrm{d}/\mathrm{d}t = \partial/\partial t + \vec{v} \cdot \nabla. \tag{13}$$

Upon substitution of this relationship in equations (10) and (11), one obtains the transformed pair of equations

$$\mathrm{d}C/\mathrm{d}t = -\tfrac{1}{2}\nabla \cdot \vec{v} \tag{14}$$

$$\mathrm{d}S/\mathrm{d}t = \tfrac{1}{2}v^2 - (Q + U) \tag{15}$$

from which the advective terms are now absent. Moreover, one can now solve for C directly, at least in a formal sense, obtaining

$$C(\vec{r}, t) = C(\vec{r}, 0) - \frac{1}{2} \int_0^t \mathrm{d}t' \, \nabla \cdot \vec{v}(\vec{r}, t') \tag{16}$$

where the integration over t' is to be performed along the (unknown) trajectory, labelled by $\vec{r}$ and $\vec{v}$. And, instead of equation (12), one has the equation of motion

$$\mathrm{d}\vec{v}/\mathrm{d}t = -\nabla(Q + U) \tag{17}$$

which is to be solved in the Lagrangian, or moving frame, provided that C, and therefore Q, can be obtained simultaneously. This is the essence of the quantum trajectory method (QTM) [4].

In practice, one simultaneously tracks an ensemble of 'particle elements', each element being labelled by values of $\vec{r}$ and $\vec{v}$, and a whole ensemble representing a single real quantum particle. The density within the ensemble must be everywhere large enough to allow for the accurate calculation of spatial gradients, up to third order, locally, i.e. in the neighbourhood of each element. This usually requires a strategy for adding and subtracting elements to and from the set being tracked, as local element densities fluctuate with time.

However, Q is again usually so badly behaved that this is also a difficult problem. In practice, even a single real particle moving in one dimension is difficult by this method, at least for interesting systems, e.g., photoionization of an initially bound electron by a weak, or moderately strong, external field. By contrast, solution of the TDSE for such a one-particle system is almost always straightforward.

For general applications involving many quantum particles, moving in three spatial dimensions, and for states evolving away from equilibrium, or for states moving between equilibria, and while retaining the formalism of the QTM, one attempts to make some progress by invoking the ansatz of Fermi molecular dynamics (FMD). By its nature, this involves some rather drastic approximations to Q.

In developing approximations to Q, one must realize that it contains all the information essential to a quantum description of what would be otherwise a purely classical problem; e.g., Q contains both the effects of the Heisenberg uncertainty principle and the Pauli exclusion principle.

There are also subsidiary conditions which any viable approximation to Q must satisfy. For example, if U contains no explicit time dependence, and if Ψ is an eigenstate of a Hamiltonian for which U is the entire potential, then [5]

$$Q = -U + \epsilon \tag{18}$$

where ϵ is the eigenenergy. Evidently, for such cases, it must then also be true that both

$$\vec{v}(\vec{r}, t) = 0 \tag{19}$$

and

$$\mathrm{d}\vec{v}(\vec{r}, t)/\mathrm{d}t = 0 \tag{20}$$

since $S = -\epsilon t$ is independent of $\vec{r}$; i.e. for a single quantum particle.

Continuing in terms of the variables already defined, one may also write, generally,

$$\vec{v}(\vec{r}, t) = \nabla S(\vec{r}, t) = \tfrac{1}{2}[\Psi^*(-\mathrm{i}\nabla)\Psi/|\Psi|^2 + \text{c.c.}] \tag{21}$$

following which the Hamiltonian itself may be written as

$$H = \tfrac{1}{2}\big[\Psi^*\big(-\tfrac{1}{2}\nabla^2\big)\Psi/|\Psi|^2 + \text{c.c.}\big] + U \tag{22}$$

or

$$H(\vec{r}, t) = \tfrac{1}{2}v^2(\vec{r}, t) + Q(\vec{r}, t) + U(\vec{r}, t). \tag{23}$$

We now consider those cases for which a purely Coulombic quantum system is initially (at $t = 0$) in an eigenstate of a time-independent Hamiltonian, while for $t > 0$ an additional time-dependent interaction ensues, namely,

$$H = H_0 + Q \tag{24}$$

$$H_0 = \sum_i p_i^2 \big/ 2m_i + U + \delta U \tag{25}$$

$$U = \sum_i \sum_{j<i} (Z_i Z_j / r_{ij}) \tag{26}$$

$$\delta U = \sum_i \delta U(\vec{r}_i, t) \tag{27}$$

for an assembly of particles labelled by i, where the system is initially in an eigenstate of $\sum_i p_i^2 \big/ 2m_i + U$.

Then, in order to be able to solve the equations of motion for the velocities and coordinates of all the particles, at every time $t > 0$ one has recourse to the following drastic approximation to Q, which is the ansatz of FMD [6]:

$$Q \equiv V_H + V_P \tag{28}$$

$$V_H = A_H \sum_i \sum_{j<i} \big(1/r_{ij}^2\big) \exp\big(-B_H r_{ij}^4 p_{ij}^4\big) \tag{29}$$

$$V_P = A_P \sum_i \sum_{j<i} \big(1/r_{ij}^2\big) \exp\big(-B_P r_{ij}^4 p_{ij}^4\big) \tag{30}$$

where, in addition to the relative spatial coordinates, relative momenta now appear,

$$r_{ij} = |\vec{r}_i - \vec{r}_j| \tag{31}$$

$$p_{ij} = |m_j \vec{p}_i - m_i \vec{p}_j| / (m_i + m_j) \tag{32}$$

and where the so-called Heisenberg and Pauli potentials, V_H and V_P, are defined.

Thus, Q is approximated by an explicit function of coordinates and momenta, of fixed algebraic form. This approximation replaces the exact Q, which is an unknown function of spatial coordinates and a functional of unknown velocities; i.e., the exact $Q(\vec{r}, t)$ depends on $C(\vec{r}, t)$, which itself depends on values of $\nabla \cdot \vec{v}(\vec{r}, t')$ for all $t' < t$.

After these preliminaries, the FMD equations of motion for a system of interacting particles can be recast as Hamilton's equations:

$$\mathrm{d}\vec{r}_i(t)/\mathrm{d}t = \nabla_{\vec{p}_i} H \tag{33}$$

$$\mathrm{d}\vec{p}_i(t)/\mathrm{d}t = -\nabla_{\vec{r}_i} H. \tag{34}$$

The purely repulsive Heisenberg potential V_H acts to stabilize the ground, and singly excited states, of multielectron atoms or ions against unphysical autoionization. V_H is allowed to operate only between electrons and nuclei. It contains two positive constants, A_H and B_H, which can be selected to match physical constraints, e.g., the binding energy of the electron, and the fact that (for $t = 0$) both $\vec{v} = 0$ and $\mathrm{d}\vec{v}/\mathrm{d}t = 0$, since $Q \sim -U$.

The purely repulsive Pauli potential V_P acts to distribute electrons bound in an atom or ion into shells. It acts only between electrons of the same 'spin'. V_P also contains two positive constants, A_P and B_P, which again can be selected to match physical constraints [6]. (For an eigenstate of a multielectron atom, the four constants can be picked to give a good representation of the total energy, and the fact that $\vec{v}_i = 0$ and $\mathrm{d}\vec{v}_i/\mathrm{d}t = 0$ for all electrons.)

For work in which precision is not essential, it has sufficed to pick the four constants A_H, B_H, A_P and B_P such that the first ionization potential, according to FMD, agrees, generally, to within 20%, with its corresponding Hartree–Fock value, for all atoms throughout the periodic table [7].

To summarize, some advantages of FMD are:

(a) Multielectron atoms and ions, in ground or singly excited states, are stabilized against unphysical autoionization by the Heisenberg potential V_H [6].
(b) Atoms and ions generally possess good values of the ionization potential [7].
(c) Multielectron atoms and ions possess a shell structure, arising from the Pauli potential V_P [6, 7].
(d) Radii of individual electronic shells are, generally, physically reasonable [7].
(e) A system of atoms, ions and electrons, all interacting, can be simulated successfully by FMD with a set of coupled ordinary differential equations. This system of atoms, ions and electrons can be inhomogeneous spatially, and exhibit time-dependent behaviour. Fluctuations about local averages are fully accessible by this method. Fluctuations can be either spatial or temporal, or both. Transport coefficients can be computed directly from the simulation.

Examples of systems which have been successfully simulated with FMD are:

(i) The dynamics of the ionization of multielectron atoms, and of clusters of atoms, by short pulse, long wavelength, laser beams has been simulated [8–10].
(ii) The equilibrium net positive charge on a fast, highly charged, nucleus has been simulated, for the case where the nucleus propagates through a gaseous medium [11].
(iii) Temperature equilibration rates for electron and ion components of a plasma initially out of equilibrium have been simulated [12].

Comparison of these FMD results with the outcome of calculations based on existing rigorous methods has not yet been accomplished, i.e. to the extent that methods such as nonequilibrium density-functional theory do indeed already exist.

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