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Toward an ab Initio Treatment of the Time-Dependent Schrödinger Equation of Molecular Systems

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The time-dependent variational principle (TDVP) is employed to produce equations of motion that approximate the time-dependent Schrodinger equation. Choices of wave function and basis sets are discussed. The use of electron translation factors and the electronic and nuclear parts of the molecular wavefunction are put in the context of the electron nuclear dynamics (END) theory. The role of wave function parameters as dynamical variables is discussed, and the use of coherent state parametrization is explored.

1. Introduction

Application of the time-dependent Schrödinger equation as is done for instance in the theory of molecular reaction dynamics has traditionally sought a description of molecular events in terms of a basis of stationary molecular electronic states and their associated potential energy surfaces. This approach often leads to attractive pictures and seeks an understanding of microscopic processes in terms of the properties of potential energy surfaces. Such descriptions of e.g. elementary chemical reactions in terms of preconstructed potential energy surfaces are omnipresent in molecular reaction dynamics. An example is the popular and widely applied transition state theory. In general, when one or more potential energy surfaces of acceptable accuracy together with the nonadiabatic coupling terms are known, the nuclear dynamics can be done classically, semiclassically, or quantum mechanically.

In spite of the many successes, this approach is undoubtedly being hindered by the lack of generally available accurate potential energy surfaces and the associated nonadiabatic coupling terms. Ab initio electronic structure theory, which generates the "best" potential energy surfaces, solves the electronic Schrödinger equation for stationary nuclei in a large number of discrete points and can similarly generate nonadiabatic coupling terms. Application of this data in molecular reaction dynamics requires some interpolation (often in many dimensions), a far from trivial task, when accurate energy values and gradients are required. The difficulties in generating full, accurate, ab initio, potential energy surfaces for general polyatomic systems have caused many dynamics treatments to rely on semiempirical surfaces, such as those obtained via the method of diatomics in molecules (DIM).

In recent years, a new set of dynamics methods have appeared that proceed without precalculated potential energy surfaces. These methods use one of three approaches: (1) the potential energy surface and its gradient is calculated on demand using conventional electronic structure methods such as self-consistent field (SCF) or Kohn−Sham density functional theory (DFT); or (2) a dynamical system in parallel with the nuclear dynamics is set up for artificial electronic degrees of freedom such that the parallel dynamics produces the state and gradient that is the same as or close to what the electronic structure methods would produce for the same geometry; or (3) a coupled dynamical system involving both the nuclear and the physical electronic degrees of freedom is constructed and solved. The first approach is now available in almost all electronic structure software. The method of Car and Parinello[1] is an implementation of the second approach and has received some notoriety in the current literature. The electron−nuclear dynamics (END) theory, which is discussed here, follows the third approach. END uses a basis different from that of stationary electronic states for solution of the dynamical equations but routinely employs stationary electronic states in the analysis of the evolving state. Even the END dynamics often follows closely one potential energy surface. This is particularly true at very low collision energies and for part of the dynamics where the stationary electronic states are well separated. In this way, END provides support for using the Born−Oppenheimer approximation in such processes. When admixtures of other states are required, the END automatically provides the correct couplings through the dynamical equations.

END is a general approach to find approximate solutions to the time-dependent Schrödinger equation. It has been described in the literature in considerable detail.[2,3] The END theory offers a hierarchy or natural progression of approximations from the simplest model of classical nuclei and a single determinantal representation of the electrons all the way to a full multiconfigurational quantum description of both electrons and nuclei.

Applications of the basic END approach have been made to a number of ion−atom and ion−molecule reactive collisions of small species in order to test the sensitivity to the choice of basis set and the overall performance in order to reach predictive accuracy. Proton collisions with atoms of hydrogen, helium, and oxygen,[3−6] and α particles with Ne atoms,[7] at energies ranging from a fraction of an eV to tens of keV (depending on the system) have been studied with calculated transition probabilities and cross sections for electron transfer and excitation in agreement with experimental results.

Ion−molecule reactive collisions have been studied with equally promising results. This includes proton collisions with H_2 molecules[4,8] at energies that involve product channels of electron transfer and vibrational excitation, as well as total

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breakup, with water molecules[9] and with methane molecules.[10] Also, H_2^+ collisions with hydrogen molecules have been studied.[11]

Model systems exhibiting intramolecular electron transfer have been treated within the simplest END approach[12] with promising results. Also, the relationship between vibrational modes of positively charged polyacetylene oligomers and soliton dynamics of polyacetylene chains has been studied.[13]

2. Electron−Nuclear Dynamics Theory

The ideas behind electron−nuclear dynamics (END) are straightforward. The theory is discussed in great detail elsewhere.[12] However, the details of the discussion so far have been limited to the simplest model, which describes the electrons by a coherent state family of determinantal wave functions and uses classical nuclei. Therefore, there is room for an explanation of the generality of the END theory attempted here.

Both the power and the limitation of END lie in the choice of the family of wave functions employed in the time-dependent variational principle (TDVP).[14] The correct choice permits the selection and emphasis of the important degrees of freedom for a given process, but any choice, of course, limits what can be achieved to that space of wave functions. Too much detail, e.g. a full representation on a grid, may lead to intractable computations, while too restrictive a choice, say classical nuclei, prohibits the description of some important aspects of the dynamics, such as multichannel dynamical branching. The flexibility of the END theory permits a balanced choice to be made for each problem studied.

The END for general reactions using a full quantum description is given in this section in a form that permits the identification of the more approximate implementation presented before as a special case.

Two rather basic observations for the choice of families of variational wave functions can be made based on experience: (1) The electronic wave function of a molecular system is approximated remarkably well by a single determinantal wave function, but the flexibility to use multiple configurations is essential. (2) The nuclei behave quite classically in many respects; however, for multichannel processes the molecular wave function must be capable of splitting into multiple packets in accordance with the superposition principle.

Our experience has shown that nonlinear families of wave functions, rather than those formed by linear superposition, often provide accurate results with greater efficiency versus effort. Although identical nuclei should be given wave functions of correct permutational symmetry, the discussion below will not treat the symmetry of the nuclei. Our own experience is that the numerical effects of nuclear permutation symmetry are often negligible and the notation becomes unduly cluttered. The expressions are easily adapted for such symmetry, when needed.

For a didactic presentation of a general framework for simultaneous dynamics of electrons and nuclei, the coordinates and the basis functions of choice could be different from those commonly used in other approaches. This does not mean that the particular choice used here is believed to perform better or worse in numerical computations, but rather that it clarifies the similarity and differences between nuclear and electronic degrees of freedom.

The symbol Ψ is used for molecular wave functions, Φ for electronic wave functions, Ξ for nuclear wave functions. A molecular wave function is given in terms of the Born−Huang[15] expansion

$$\Psi(X,x,c,f,d,e,z,R,P) = \sum_n c_n \Xi_n(X,f,d,R,P)\, \Phi_n(x,e,z,R,P) \tag{1}$$

where the various parameters are time-dependent and explained below.

Nuclear Wave Function. Each nuclear wave function in the above expansion represents all nuclei in the system and is a sum

$$\Xi_n(X,f,d,R,P) = \sum_{(\pi)} f_n(\pi) \prod_{l=1}^{N_{\mathrm{at}}} \chi_{\pi(l)}(\vec{X}_l,d,\vec{R}_l,\vec{P}_l) \tag{2}$$

of products of orbitals

$$\chi_l(\vec{X},d,\vec{R},\vec{P}) = \sum_j d_{lj} X^{k_{lj}} Y^{m_{lj}} Z^{n_{lj}} \exp[-\alpha_{lj}(\vec{X}-\vec{R})^2 - i\vec{P}\cdot\vec{X}] \tag{3}$$

centered on average locations R with average momenta P. The index (π) stands for the set of indices π_l, $l = 1, ..., N_{\mathrm{at}}$ with N_{at} the number of atomic nuclei. This sum describes the correlation between the nuclei.

It is well-known that the major part of this correlation for any bound subsystem is described by vibrational eigenstates of normal-mode coordinates. For example, for a diatomic molecule in the vibrational groundstate with a sharp localization in orientation (θ, φ), the wave function has the form

$$\begin{aligned}&\exp[-\alpha(\vec{X}_{\mathrm{cm}} - \vec{C})^2 - \beta(X_{\mathrm{rel}} - D)^2]f(\theta, \varphi) = \\ &\exp[-\alpha(\vec{X}_{\mathrm{cm}} - \vec{C})^2 - \beta(\vec{X}_{\mathrm{rel}} - \vec{D})^2] = \exp[-\gamma(\vec{X}_1 - \vec{R}_1)^2 - \\ &\gamma(\vec{X}_2 - \vec{R}_2)^2 - \delta(\vec{X}_1 - \vec{R}_1)\cdot(\vec{X}_2 - \vec{R}_2)] = \\ &\exp[-\gamma(\vec{X}_1 - \vec{R}_1)^2]\exp[-\gamma(\vec{X}_2 - \vec{R}_2)^2]\sum_n[-\delta(\vec{X}_1 - \vec{R}_1)\cdot \\ &(\vec{X}_2 - \vec{R}_2)]^n/n!\end{aligned} \tag{4}$$

where in the second step the angular localization is given a Gaussian form, and where

$$\begin{aligned}\gamma = \alpha/4 + \beta, \quad \delta = \alpha/2 - \beta \\ \vec{C} = (\vec{R}_1 + \vec{R}_2)/2, \quad \vec{D} = \vec{R}_1 - \vec{R}_2\end{aligned} \tag{5}$$

This shows the sum in terms of products of orbitals for nuclei. The correlation can be seen to need basis functions with high angular momentum components k, m, and n for eq 3 to converge.

Quantum mechanical treatments of nuclear dynamics on molecular potential energy surfaces often employ basis functions in internal coordinates that are carefully chosen to be close, but not identical, to normal modes so as to accelerate convergence. For example, the discrete variable representation (DVR) method typically selects from 6 to 12 discretization points in angular variables, which corresponds to a polynomial fit of the same order. This would in the above expansion correspond to basis functions with $k + m + n$ ranging from 6 to 12 or more, because the generic basis functions (eq 3) are not as optimal as is customary with internal variables for quantum molecular dynamics.

Electronic Wave Function. Each electronic wave function in the expansion (1) may be represented as a sum of determinants

$$\Phi_n(x,e,z,R,P) = \sum_{(\pi)} e_{n(\pi)} \det[\varphi_{\pi(h)}(\vec{x}_g,z,\vec{R},\vec{P})] \tag{6}$$

built of orbitals

$$\varphi_h(\vec{x},z,\vec{R},\vec{P}) = \sum_p z_{ph} x^{k_{ph}} y^{m_{ph}} z^{n_{ph}} \exp[-\alpha(\vec{x} - \vec{R})^2] \quad (7)$$

centered on average nuclear positions R moving with the same average velocity P/M as the nuclei. The symbol (π) is a configuration label and runs over the list of configurations. The sum describes the correlation between electrons.

It is well-known that the best single determinant, constructed with the self-consistent field (SCF) method, provides a reasonable description for most systems. For computational efficiency we choose Gaussian type orbitals, but obviously it is possible to use other types of orbitals, even numerical representations on a grid, if that is needed and judged to be computationally feasible for the problem under consideration. It is not unusual in correlated electronic structure theory to use angular momentum basis functions through f and g types or higher and to use basis sets of so-called double-zeta, triple-zeta, or even better quality. The questions of the quality of basis set needed for END applications to reach converged results are largely still unanswered, but initial studies on systems with first-row elements seem to indicate that converged results are obtained with quite limited basis sets. Further studies are needed of the behavior of the calculated results as functions of increasing electronic basis.

Molecular Wave Function. In some general approach to determine a total molecular wave function, the coefficients d and c of the nuclear wave function could be determined to a good approximation, for instance, by finding the eigenstates in nuclear normal coordinates, while the coefficients e and z of the electronic wave function could be obtained by SCF plus any one of a number of well-proven correlated electronic structure methods. It must be emphasized that this is *not* what END does, as elaborated below.

The sum in the wave function equation (1) describes the correlation between the electrons and the nuclei. It is well-known that the Born−Oppenheimer (BO) approximation provides an excellent first term in the sum. In that case the electronic wave function is the eigenfunction with eigenvalue $V(X)$ of the electronic problem with the nuclei frozen at the geometry X. And the nuclear wave function is the vibrational−rotational eigenfunction of the nuclei moving on the molecular potential surface $V(X)$. Because of the overwhelming success of the BO approximation, most approaches to molecular dynamics include the construction of the potential energy surface to some acceptable level of accuracy.

Because it is technically not (yet) feasible to express the matrix elements of the nuclear Hamiltonian in the BO approximation directly in terms of the nuclear basis functions (eq 3) and the electronic basis functions (eq 7), all molecular dynamics methods proceed through fitting some analytic function to the potential energy surface. This is already starting to change, as shown by the popularity of gradient-driven molecular dynamics and Car−Parinello-like methods. These methods employ classical (Newtonian) dynamics of the nuclei but use gradients supplied directly by electronic structure methods rather than from analytic fitted forms as was still the norm only a decade ago.

Instead of the classical Born−Oppenheimer or adiabatic form of the wave function

$$\Psi(X,x,f,d,e,z,R,P) = \Xi(X,f,d,R,P)\,\Phi(x,e,z,X) \quad (8)$$

where the electronic wave function depends parametrically on the nuclear dynamical variables X, END considers a sum (eq 1) of less tightly coupled products of nuclear and electronic wave functions where the BO approximation and potential energy surface are only defined for the average nuclear positions R and momenta P. This series bears some resemblance to the diabatic form of the Born−Huang expansion, which is known to be formally equivalent to the adiabatic or BO form and to be more rapidly converging near avoided crossings of surfaces.

Electron−Nuclear Dynamics. Because the goal is to study dynamics in a time-dependent method, it is not necessary to require the convergence of both the electronic and the nuclear wave functions in each molecular term separately. Rather, it is sufficient to consider convergence for the electron nuclear dynamics of the molecular system with a wave function expressed directly as a sum of basic configurations

$$\Psi(X,z,c,d,z,R,P) = \sum_{(\pi)} c_{(\pi)} \prod_{i=1}^{N_{\rm at}} \chi_{\pi(i)}(\vec{X}_i,d,\vec{R}_i,\vec{P}_i) \times \det[\varphi_{\pi(h)}(\vec{x}_g,z,\vec{R},\vec{P})] \quad (9)$$

where the symbol (π) now runs over all combined electron−nuclear configurations.

The coefficients c now describe the correlation among electrons (MCSCF), among the nuclei (normal-mode states), and between electrons and nuclei (Born−Oppenheimer states) and become (time-dependent) dynamical variables. Note that the entire wave function depends parametrically on the average nuclear positions R and momenta P. When the basis is complete, this is largely irrelevant as the average values can be computed from the wave function. It is a well-known technique for accelerating convergence of numerical solutions of differential equations, to make the basis-function placement part of the solution method. Examples are found in the placing of the electronic basis functions on the nuclear centers in electronic structure, or using carefully chosen internal coordinates in quantum molecular dynamics, or employing adaptive grid methods in fluid dynamics. By making the parameters R and P dynamical variables, the basis functions are made to follow the flow of the dynamics such that accurate solutions can be constructed with a more limited basis set.

Analogous to the classical mechanics, there is a quantum mechanical "Hamilton's principle" or time-dependent variational principle (TDVP). The quantum mechanical action[14] is defined to be

$$A = \int_{t_1}^{t_2} L(\Psi^*,\Psi)\,{\rm d}t \quad (10)$$

where the quantum mechanical Lagrangian is

$$L(\Psi^*,\Psi) = \left\langle \Psi \middle| i\frac{\partial}{\partial t} - H \middle| \Psi \right\rangle / \langle \Psi | \Psi \rangle \quad (11)$$

and H is the quantum mechanical Hamiltonian of the system. The many-body wave function Ψ is subject to the boundary conditions

$$\delta|\Psi\rangle = \delta\langle\Psi| = 0 \quad (12)$$

at $t = t_1$ and t_2. TDVP yields the time-dependent Schrödinger equation if Ψ is varied in the full Hilbert space. If, however, the variations are restricted to a predetermined region of Hilbert space, as it would be for a Ψ chosen to be of a specific form, then the Lagrangian will generate an approximate time evolution. The notation $\Psi \equiv \Psi(\zeta) \equiv |\zeta\rangle$ is introduced, with $\zeta = \{\zeta_1, \zeta_2,$

..., $\zeta_M\}$ being a (column) array of complex parameters $\zeta_\alpha \equiv \zeta_\alpha(t)$ depending on the time parameter t.

The variation principle states that

$$\delta A = \delta \int_{t_1}^{t_2} L \, \mathrm{d}t = 0 \tag{13}$$

and using integration by parts and the boundary conditions (12), the surviving terms of δL can be written as

$$i\frac{\langle \delta\zeta|\dot{\zeta}\rangle}{\langle \zeta|\zeta\rangle} - \frac{\langle \delta\zeta|H\zeta\rangle}{\langle \zeta|\zeta\rangle} - i\frac{\langle \delta\zeta|\zeta\rangle}{\langle \zeta|\zeta\rangle^2}\langle \zeta|\dot{\zeta}\rangle + \frac{\langle \delta\zeta|\zeta\rangle}{\langle \zeta|\zeta\rangle^2}\langle \zeta|H\zeta\rangle + \text{complex conjugate} \tag{14}$$

where the notation $\mathrm{d}\zeta/\mathrm{d}t = \dot{\zeta}$ is used.

In order to obtain the dynamical equations, the notations $S(\zeta^*, \zeta) = \langle \zeta|\zeta\rangle$ and $E(\zeta^*, \zeta) = \langle \zeta|H\zeta\rangle/\langle \zeta/\zeta\rangle$ are introduced, which lead to

$$\delta A = \int_{t_1}^{t_2} \left\{ \sum_\beta \left[-i \sum_\alpha \left(\frac{\partial^2 \ln S}{\partial \zeta_\alpha^* \, \partial \zeta_\beta} \dot{\zeta}_\alpha^* - \frac{\partial E}{\partial \zeta_\beta} \right) \delta\zeta_\beta + i \sum_\alpha \left(\frac{\partial^2 \ln S}{\partial \zeta_\alpha \, \partial \zeta_\beta^*} \dot{\zeta}_\alpha - \frac{\partial E}{\partial \zeta_\beta^*} \right) \delta\zeta_\beta^* \right] \right\} \mathrm{d}t = 0 \tag{15}$$

and since $\delta\zeta_\beta$ and $\delta\zeta_\beta^*$ are independent variations one can write

$$i \sum_\beta C_{\alpha\beta} \dot{\zeta}_\beta = \frac{\partial E}{\partial \zeta_\alpha^*} \tag{16}$$

where the complex Hermitian matrix $\mathbf{C} = \{C_{\alpha\beta}\}$ with elements $C_{\alpha\beta} = \partial^2 \ln S/\partial\zeta_\alpha^*\partial\zeta_\beta$.

For two differentiable functions $f(\zeta, \zeta^*)$ and $g(\zeta, \zeta^*)$ the generalized Poisson bracket

$$\{f, g\} = -i \sum_{\alpha,\beta} \left[\frac{\partial f}{\partial \zeta_\alpha} (\mathbf{C}^{-1})_{\alpha\beta} \frac{\partial g}{\partial \zeta_\beta^*} - \frac{\partial g}{\partial \zeta_\alpha} (\mathbf{C}^{-1})_{\alpha\beta} \frac{\partial f}{\partial \zeta_\beta^*} \right] \tag{17}$$

is defined. It follows that $\dot{\zeta} = \{\zeta, E\}$ and $\dot{\zeta}^* = \{\zeta^*, E\}$, i.e., the time evolution of wave function parameters is governed by Hamilton-like equations.

The generalized phase space and the associated Poisson bracket (eq 17) permit the relations

$$\{\zeta_\alpha, \zeta_\beta\} = \{\zeta_\alpha^*, \zeta_\beta^*\} = 0; \quad \{\zeta_\alpha, \zeta_\beta^*\} = -i(\mathbf{C}^{-1})_{\alpha\beta} \tag{18}$$

which show that ζ^* and ζ behave as "classical" coordinates and momenta. If the matrix $\mathbf{C}$ was the unit matrix the corresponding phase space would be canonical or "flat". However, in general this generalized phase space is curved.

Dynamical Variables and Wave Function Parameters. The wave function parameters are the dynamical variables, the evolution of which is governed by the dynamical equations. Because of this it is essential that the parametrization is nonredundant, that the parameter manifold is continuous, and that it is complete. Such requirements lead to the consideration of coherent states[16] or at least to families of state vectors whose parameters have these properties. The completeness of a family of state vectors $|\zeta\rangle$ can be expressed through the resolution of the identity I

$$\int |\zeta\rangle\langle\zeta| \, \mathrm{d}\zeta = I \tag{19}$$

with some appropriate positive measure $\mathrm{d}\zeta$ defined on the parameter space.

The importance of this type of parametrization and an important consequence of the completeness is that during the evolution the dynamics should, if required, be able to pass through any one of the members of the family $|\zeta\rangle$. In order to accomplish this in practice one needs the capability to switch from a current local parametrization or chart that for some reason has led to, say, too large parameter values and therefore numerically unstable dynamical equations, to another chart that is more suitable for that part of the dynamics. Such switching of charts must be done without any artificial discontinuities in trajectories and various properties, a behavior that can be guaranteed with appropriate parametrization. An example of this is a Thouless parametrization of a determinantal electronic wave function $|\mathbf{z}\rangle = \det\{\chi_i(x_j)\}$, with the spin orbitals expressed in terms of atomic spin orbitals $\{u_k(x_l)\}$ centered on the various nuclei, as

$$\chi_i = u_i + \sum_j u_j z_{ji} \tag{20}$$

with time-dependent complex coefficients z_{ji} being the dynamical variables. This parametrization guarantees that all possible determinants in terms of the atomic orbitals is accessible during a dynamical evolution.

As an example of how this works we consider a particular trajectory of the $\mathrm{H} + \mathrm{H}_2\ (0, 0) \rightarrow \mathrm{H}_2(v, j) + H$ exchange reaction at an energy of 1.2 eV in the center of mass frame. Using an atomic orbital basis and a representation of the electronic state in terms of a Thouless determinant and a classical description of the protons, the leading term of the electronic state of the reactants is

$$|(1\mathrm{s}_1 + 1\mathrm{s}_2)\alpha(1\mathrm{s}_1 + 1\mathrm{s}_2)\beta_1\mathrm{s}_3\alpha| \tag{21}$$

where 1 and 2 label the protons of the reactant molecule, 3 denotes that of the projectile atom, and $1\mathrm{s}_i$ is an atomic orbital centered on proton i.

The reactive trajectory proceeds by exchange of protons 2 and 3, making the leading term of the product electronic state

$$|(1\mathrm{s}_1 + 1\mathrm{s}_3)\alpha(1\mathrm{s}_1 + 1\mathrm{s}_3)\beta 1\mathrm{s}_2\alpha| \tag{22}$$

The original chart or Thouless parametrization

$$\begin{aligned} &1\mathrm{s}_1\alpha + 1\mathrm{s}_2\alpha z_1 + 2\mathrm{s}_1\alpha z'_1 + ... \\ &1\mathrm{s}_2\beta + 1\mathrm{s}_1\beta z_2 + 1\mathrm{s}_3\beta z'_2 + ... \\ &1\mathrm{s}_3\alpha + 1\mathrm{s}_2\alpha z_3 + 2\mathrm{s}_1\alpha z'_3 + ... \end{aligned} \tag{23}$$

will then become unsuitable since, say, the absolute value of the z-coefficients of the $1\mathrm{s}_2\alpha$ spin orbital become large in comparison to unity, making the integration of the dynamical equations less accurate. The ENDyne code which implements the END theory automatically switches to a new chart with the new coefficients suitable for the product side. Although the leading determinant in the basis thus has changed, the total END wave function is the same and the resulting trajectory shows no discontinuous behavior.

3. Implementation of the Electron−Nuclear Dynamics Theory

The integration of the END equations from a given set of initial conditions, the projection of the evolved state vector on a given (final) state to obtain state to state transition probabilities, the calculation of cross sections (differential and integrated) including the semiclassical corrections to classical results, and the necessary interface to provide graphic representations of the evolution of various properties are all accomplished within the ENDyne code.[17]

As seen in the previous section, the TDVP produces an approximation to the time-dependent Schrödinger equation in the form of a system of coupled first-order ordinary differential equations. Methods for integrating such systems are available in the literature[18] and the modification and implementation of such techniques in the ENDyne code has been discussed in some detail elsewhere.[12]

An initial molecular state is usually determined by an optimization algorithm to determine the initial values of the electronic and nuclear parameters. For instance, the optimal Thouless parametrization of an electronic state is one for which the z-parameters are as small as possible. Here one should note that the initial state of the total system can contain a projectile moiety with both nuclei and electrons being translated toward a target molecule. This requires some care in specifying the initial conditions in order to obtain a proper dynamics.

When electrons are also allowed to evolve dynamically, i.e., without the use of a precalculated or fitted potential energy surface, then a basis set, much like in electronic structure theory, is used. It was shown some time ago[19] how to account for the electron dynamics when an atom or molecule is in motion. The idea is to use an exponential factor in the atomic or molecular orbital basis to account for the momentum of the electrons explicitly. The exponential factors are called electron translation factors (ETF). A simple example is that of the ground state of a moving H atom (using atomic units)

$$\psi(\vec{r}) = \exp(i\vec{v}\cdot\vec{r} - i(\vec{v}^2/2 - \epsilon_{1s}))\phi_{1s}(\vec{r} - \vec{R}) \qquad (24)$$

which satisfies the time-dependent Schrödinger equation. In order to use ETF's for computations in the dynamics studies of molecular systems, a general, high-quality integral package must be written which includes basis orbitals with ETF's such as the following Gaussian basis set

$$\varphi_h(\vec{x},z,\vec{R},\vec{P}) = \sum_p z_{ph} x^{k_{ph}} y^{m_{ph}} z^{n_{ph}} \exp[-\alpha(\vec{x} - \vec{R})^2 - \mathrm{im}/M\vec{P}\cdot\vec{x}] \qquad (25)$$

Such a tool does not yet exist, although some attempts have been made to produce a general integral package.[20] Much work continues to be done on the topic of ETF's in the area of atomic and molecular collisions. It is not the purpose of this paper to review the important advances made in this area, but to explain the different approach to the challange of ETF's adopted in the current implementation of the END theory using standard integral packages such as HERMIT.[21,22]

We review the END equations for the simplest model of classical nuclei and a single complex determinantal wave function for the electrons, and we identify the electron−nuclear couplings which are responsible for the need to introduce ETF's. The modified Fock operator with these couplings included yields an equation that determines atomic or molecular orbitals with the correct translational properties within the given basis. This equation is the "boosted SCF" equation. The solutions are complex, linear combinations of atomic basis functions, which constitute the best approximation to the ETF's within the basis and have the property of not changing in time as long as they are in inertial motion.

ETF's are always needed, even for low energies, to obtain correct dynamics. However, they can be introduced as a complex expansion in terms of real orbitals or as explicit exponential factors multiplying the atomic or molecular orbitals. When the original (real) orbitals basis is small, the explicit factor provides more accurate results and the complex expansion needs a larger basis to get to the same level of accuracy. This becomes increasingly relevant for high kinetic energies, say above a few keV. For most processes at kinetic energies in the range up to few hundred eV's, the complex expansion approach within a modest basis set provides an excellent dynamical description.

END uses the time-dependent variational principle as a unifying principle to derive the dynamic equations for the wave function parameters, which as shown above constitute the dynamical variables of the system. The use of the TDVP allows the equations of motion to apply not only for a fully quantal or completely classical treatment but also for a mixed quantum-classical description. For basis functions which depend, in some form, on the classical dynamical variables (e.g. basis functions centered on classical nuclei and thus depend on their positions and momenta), this approach explicitly introduces all nonadiabatic couplings between the classical and quantum degrees of freedom. These couplings are essential for satisfying conservation theorems and for correct behavior of many observable quantities.[5,23]

Approximate dynamical equations are obtained by making specific choices of the form of wave function to use and which degrees of freedom to treat classically. For this argument we choose classical atomic nuclei and position electronic basis functions on the dynamically moving nuclei. A single Thouless determinant[24] is used to describe the electrons.

The Lagrangian that encompasses these approximations is

$$L = \frac{1}{2}\sum_k (\vec{P}_k\cdot\dot{\vec{R}}_k - \dot{\vec{P}}_k\cdot\vec{R}_k) - \sum_k \frac{\vec{P}_k^{\,2}}{2M_k} + \left\langle z\left|\frac{i}{2}\left(\frac{\mathrm{d}}{\mathrm{d}t} - \frac{\tilde{\mathrm{d}}}{\mathrm{d}t}\right) - H_{\mathrm{el}}\right|z\right\rangle / \langle z|z\rangle \qquad (26)$$

where the symmetric form of the time derivative includes the operator $\tilde{\mathrm{d}}/\mathrm{d}t$ acting on the bra and where the electronic Hamiltonian H_{el} contains the nuclear−nuclear repulsion potential energy. The symbols $\vec{R}_k$, $\vec{P}_k$, and M_k denote the position, momentum, and mass, respectively, of nucleus k, while $\dot{\vec{R}}$ and $\dot{\vec{P}}$ are the time derivatives of said quantities. The electronic wave function $|z\rangle$ depends on a number of complex parameters, such as molecular orbital coefficients, collectively denoted by z. The TDVP means that the action must be stationary as expressed by eq 13.

In order for the phase space of the electrons to be well-defined and so the electron can carry momentum the wave function must be complex. Standard normalized molecular orbital (MO) coefficients are redundant, which can be seen from the fact that rotations separately among occupied and unoccupied states do not change the state. Such a choice of MO coefficients as dynamical parameters makes the equations singular. Thouless[24] developed a set of nonredundant parameters z for a single determinant. They turn out to be the coset representatives of the unitary group $U(K)$ and belong to the coset space $U(K)/U(N) \times U(K - N)$, where N is the number of electrons and K is the rank of the basis. Single determinants parametrized this way are coherent states.[12,14,16] The important features of these parameters from the point of view of dynamics is that they provide a complex, continuous, nonredundant wave function parametrization. The complex parameters are actually dynamical variables and form a (generalized) phase space with a nonunit metric and a generalized Poisson bracket.[14]

In terms of a given spin orbital basis set $\{\phi_i;\ i = 1, \mathrm{K}\}$ centered on the nuclei, the occupied orbitals of the determinant are

$$\chi_h = \phi_h + \sum_{p=N+1}^{K} z_{ph}\phi_p \tag{27}$$

The first N orbitals ϕ_h form the reference determinant. If the basis is orthogonal, the virtual dynamical orbitals are written in terms of the same coefficients as

$$\chi_p = \phi_p - \sum_{h=1}^{N} z^*_{ph}\phi_h \tag{28}$$

In terms of a nonorthogonal basis the virtual dynamical orbitals are

$$\chi_p = \phi_p + \sum_{h=1}^{N} v^*_{hp}\phi_h \tag{29}$$

where the v coefficients are functions of the complex, time-dependent z-coefficients.[3,12] The orbitals χ_h are mutually non-orthogonal as are the χ_p, but they satisfy $\langle\chi_p|\chi_h\rangle = 0$.

In terms of these dynamical parameters for electrons and nuclei, the TDVP yields the dynamical equations in matrix form

$$\begin{pmatrix} iC & 0 & iC_R & 0 \\ 0 & -iC^* & -iC_R^* & 0 \\ iC_{\mathrm{R}}^\dagger & -iC^T & C_{RR} & -I \\ 0 & 0 & I & 0 \end{pmatrix} \begin{pmatrix} \dot{z} \\ \dot{z}^* \\ \dot{\vec{R}} \\ \dot{\vec{P}} \end{pmatrix} = \begin{pmatrix} \partial E/\partial z^* \\ \partial E/\partial z \\ \partial E/\partial \vec{R} \\ \partial E/\partial \vec{P} \end{pmatrix} \tag{30}$$

where the total energy is

$$E = \sum_k \frac{{P_k}^2}{2M_k} + \frac{\langle z|H_{\mathrm{el}}|z\rangle}{\langle z|z\rangle} \tag{31}$$

The coupling elements in eq 30 are

$$\begin{aligned} C &= \frac{\partial^2 \ln S(z^*,\vec{R}',z,\vec{R})}{\partial z^*\,\partial z}\Big|_{\vec{R}=\vec{R}'} \\ C_R &= \frac{\partial^2 \ln S(z^*,\vec{R}',z,\vec{R})}{\partial z^*\,\partial R}\Big|_{\vec{R}=\vec{R}'} \\ C_{RR} &= -2\,\mathrm{Im}\frac{\partial^2 \ln S(z^*,\vec{R}',z,\vec{R})}{\partial R'\,\partial R}\Big|_{\vec{R}=\vec{R}'} \end{aligned} \tag{32}$$

They are derived from the overlap

$$S(z^*,\vec{R}',z,\vec{R}) = \langle z;\vec{R}'|z;\vec{R}\rangle \tag{33}$$

formed between Thouless determinants at two different geometries $\vec{R}'$ and $\vec{R}$.

It is noteworthy that using the TDVP ensures the conservation of important physical quantities such as total energy, total momentum, and total angular momentum.[3,12] The coupling terms in the dynamical metric play a cruicial role in this connection. An SCF approach that includes the coupling terms C_R can be introduced. For a molecule or atom in inertial motion, the nuclear acceleration will be zero, but $\dot{\vec{R}}$ will not be. Thus, if initial z coefficients corresponding to some stationary state are used, they will change in time because of the electron−nuclear coupling C_R. When ETF's are explicit factors built into the basis, extra terms appear on the right side of the electronic equations which cancel these coupling terms.[19] In most current approaches the ETF's are dropped in the evaluation of the two-electron Coulomb repulsion integrals, a procedure that can often be justified as long as the electron deBroglie wavelength is long compared to the orbital size. Alternatively, by allowing for complex orbital coefficients, as is done in the END theory, one relies on the basis to approximate the ETF's and then the ETF is included in all integrals.

A straightforward way to see how the coupling terms generate the ETF is in the SCF approach that includes the coupling terms. Phrasing the problem in this way means that a set of z's are sought that for given velocities $\dot{\vec{R}}_k = \vec{V}_k$ satisfy $\dot{z}_{ph} = 0$. Imposing this condition means that the equations to be solved are

$$i\sum_k C_{\vec{R}_k}\cdot\vec{V}_k = \partial E/\partial z^* \tag{34}$$

which can be written in matrix form as[12]

$$0 = (-\mathbf{z} \quad \mathbf{I}^\circ)\{\langle\phi_i|\hat{F} - i\sum_k \vec{V}_k\cdot\nabla_{\vec{R}_k}|\phi_j\rangle\}\begin{pmatrix}\mathbf{I}^\bullet \\ \mathbf{z}\end{pmatrix} \tag{35}$$

where $\hat{F}$ is the ordinary Fock operator, ϕ_k are the basis functions, assumed for present purposes with no loss of generality to be orthonormal, the columns of the partitioned matrix

$$\begin{pmatrix}\mathbf{I}^\bullet \\ \mathbf{z}\end{pmatrix}$$

are the occupied molecular orbital coefficients, and the columns of

$$(-\mathbf{z} \quad \mathbf{I}^\circ)^\dagger = \begin{pmatrix}-\mathbf{z}^\dagger \\ \mathbf{I}^\circ\end{pmatrix}$$

are the virtual molecular orbital coefficients. The symbols $\mathbf{I}^\bullet$ and $\mathbf{I}^\circ$ denote the unit matrices of dimension N and $K - N$, respectively.

Without the nuclear gradient term, this is precisely the SCF equation of electronic structure theory. The added term produces an SCF scheme in a Galilei boosted frame when all velocities $\vec{V}_k$ are equal. Obviously, the extra terms will make the molecular coefficients complex. If the velocities of all the atoms are the same, then the new operator, $\hat{F} - i\vec{V}\cdot\sum_k\nabla_{\vec{R}_k}$ is Hermitian. If for some reason one wanted to find a state in initial electronic equilibrium (i.e. $\dot{z}_{ph} = 0$) but with atoms with different velocities, then the new operator would not be Hermitian, unless the overlap vanishes between orbitals belonging to nuclei with different velocities. Equation 35 with this modified Fock operator is called the boosted SCF equation.

Solution procedures for the boosted SCF equations have been added to the ENDyne code.[17] This provides the facility to obtain properly boosted starting z-coefficients. Analogous treatment can be adopted for more general wave functions.

References and Notes

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