Complete Electron Nuclear Dynamics

Erik Deumens and Yngve Öhrn*

Quantum Theory Project, University of Florida, Gainesville, Florida 32611-8435

Received: October 17, 2000; In Final Form: December 27, 2000

The Electron nuclear dynamics (END) theory is a time-dependent, nonadiabatic approach to molecular processes. It has been implemented in the ENDyne code at the level of approximation that treats the nuclei as classical particles and represents the electrons with a single complex spin unrestricted determinant. This level of theory has been successfully applied to a wide range of ion−atom and ion−molecule reactive collisions. In this paper the extensions of the END theory are outlined in some detail through a hierarchy of approximations to the level of full quantum mechanical treatment of all participating particles.

1. Introduction

This paper is dedicated to William H. Miller. It is a pleasure to acknowledge his kind interest and support of our work over many years. Electron Nuclear Dynamics (END) theory[1] has from its beginning been considered a general approach to molecular processes. However, its implementation in the ENDyne code[2] is limited to the simplest approximation of electrons being described by a single complex Thouless determinant,[3] and the atomic nuclei as classical particles in the narrow wave packet limit. Several applications have shown that this simple non-adiabatic approximation captures much of the physics of atomic and molecular reactive processes,[4−21] but is has also become clear that there are limitations to this level of treatment, particularly of a conceptual nature.

In this paper we formulate the details of a complete END implementation with all particles treated quantum mechanically, and allowing for the possibility of full correlation between electrons and between electrons and nuclei. This is done via a complete active space (CAS) approach for the electrons, and full nonadiabatic Born-Huang treatment.

Quantum mechanics appears in many guises, such as Schrödinger amplitudes, Heisenberg matrices, Wigner phase space distributions, or Feynman path integrals. END employs the phase space view that emerges from the use of coherent states[22] and that may be called the Ehrenfest representation.[17] Instead of focusing on the linearity of Hilbert space and on representations in terms of stationary states, the Ehrenfest representation emphasizes nonlinear wave function parameters as dynamical variables. The Schrödinger equation then takes the form of an infinite dimensional Hamiltonian system of equations on this parameter phase space. This formulation readily permits full quantum description as well as mixed classical quantum descriptions, such as the simplest END approximation.

It is important to note a couple of points that must be addressed. (i) The implementation of the dynamics of a complicated wave packet should be such that it reduces to classical particle motion, when the quantum mechanical degrees of freedom are left off. Heller[23−27] has introduced such a description with Gaussian wave packets, and we are using an extension of his approach. This capability is needed to describe quantum mechanical nuclei in a phase space representation. It has the added benefit when used for electrons that it allows END to describe electron−molecule scattering, as well as recombination and ionization processes. (ii) The implementation also needs to be general enough to allow for static correlation (i.e., correlated treatment of electronic and nuclear initial and final states) as well as propagation of correlated state vectors. This problem has been addressed formally in the context of END[28] for electrons. It needs further details and generalizations to include nuclear dynamics.

Cederbaum, Köppel, and Manthe[29,30,31] have developed methodology with the same goals as complete END, i.e., full quantum mechanical description of all particles in a molecular process. Such full quantum treatments are very demanding on computer time and resources, and are therefore limited to small systems. This is the main reason for why a complete END approach has not yet been implemented. However, it is our view that significant progress can be made toward efficient implementation of complete END by drawing on the techniques of linear scaling, local correlation, and the local density approximation (with or without gradient corrections) of density functional theory (DFT). We leave the details of such treatments to another paper, and limit our discussion here to a more conventional implementation.

It is perhaps worthwhile to again emphasize that the END phase space representation naturally leads to a description in terms of nonorthogonal basis states. Conventional quantum mechanical treatments often prefer orthogonal basis states and the use of stationary state representations. While such representations are natural in the study of, say, absorption or emission spectroscopy they are less obvious in dynamics. Modem femtosecond experiments seem to show that stationary states are more the exception than the rule. Furthermore, actual calculations often show that the use of nonorthogonal basis states for configuration interaction (CI) and multiconfigurational self-consistent field (MCSCF) can obtain accuracy comparable to that obtained with orthonormal basis states with expansions of orders of magnitude fewer terms. Therefore, the implementation of complete END will employ a nonorthogonal representation. Occasionally an intermediate step may be taken with an orthogonal representation, but the final expressions are just what Nature seems to like: a mess of coupled dynamical variables in a curved phase space.

In the next section the basic END approximation is briefly presented. The following section deals with the treatment of free electrons in atomic and molecular dynamics. Then general

10.1021/jp003824b CCC: $20.00

END theory is introduced and classified according to classical and quantum nuclei and also according to single electron configuration versus multiconfigurational treatments.

2. The Basic END Approximation

The lowest level of approximation in the treatment of molecular processes within the Electron Nuclear Dynamics (END) theory consists of a single determinantal description of the electrons and a classical or narrow wave packet description of the nuclei. This means that the molecular wave function can be expressed as

$$|\Psi(t)\rangle = |R(t), P(t)\rangle |z(t), R(t), P(t)\rangle \tag{1}$$

where

$$\langle X|R(t), P(t)\rangle = \prod_k \exp\left[-\frac{1}{2}\left(\frac{X_k - R_k}{b}\right)^2 + iP_k \cdot (X_k - R_k)\right] \tag{2}$$

and

$$\langle x|z(t), R(t), P(t)\rangle = \det\{\chi_i(\mathbf{x}_j)\} \tag{3}$$

with

$$\chi_i = u_i + \sum_{j=N+1}^{K} u_j z_{ji}(t) \tag{4}$$

and where the atomic spin−orbitals $\{u_i\}_1^K$ in a travelling Gaussian basis

$$(x - R_x)^1 (y - R_y)^m (z - R_z)^n \exp\left[-a(\mathbf{x} - \mathbf{R})^2 - \frac{i}{\hbar M}\mathbf{P} \cdot (\mathbf{x} - \mathbf{R})\right] \tag{5}$$

are centered on the average nuclear positions $\mathbf{R}$ moving with velocity $\mathbf{P}/M$.

The Lagrangian in the narrow nuclear wave packet limit is simply

$$L = \sum_{j,l}\left\{\left[P_{jl} + \frac{i}{2}\left(\frac{\partial \ln S}{\partial R_{jl}} - \frac{\partial \ln S}{\partial R'_{jl}}\right)\right]\dot{R}_{jl} + \frac{i}{2}\left(\frac{\partial \ln S}{\partial P_{jl}} - \frac{\partial \ln S}{\partial P'_{jl}}\right)\dot{P}_{jl}\right\} + \frac{i}{2}\sum_{p,h}\left(\frac{\partial \ln S}{\partial z_{ph}}\dot{z}_{ph} - \frac{\partial \ln S}{\partial z^*_{ph}}\dot{z}^*_{ph}\right) - \sum_{j,l}\frac{P_{jl}^2}{2M_l} - E \tag{6}$$

where $S = \langle z, R', P'|z, R, P\rangle$ and E is the electronic energy including the nuclear−nuclear repulsion terms. The Euler−Lagrange equations

$$\frac{\mathrm{d}}{\mathrm{dt}}\frac{\partial \mathrm{L}}{\partial \dot{\mathrm{q}}} = \frac{\partial \mathrm{L}}{\partial \mathrm{q}} \tag{7}$$

yield the dynamical equations for the dynamical variables $q = R_{jk}$, P_{jk}, z_{ph}, and z^*_{ph}, such that we can write

$$\begin{bmatrix} i\mathbf{C} & 0 & i\mathbf{C}_{\mathrm{R}} & i\mathbf{C}_{\mathbf{P}} \\ 0 & -i\mathbf{C}^* & -i\mathbf{C}^*_{\mathbf{R}} & -i\mathbf{C}^*_{\mathbf{P}} \\ i\mathbf{C}^\dagger_{\mathrm{R}} & -i\mathbf{C}^{\mathrm{T}}_{\mathbf{R}} & \mathbf{C}_{\mathbf{RR}} & -\mathbf{I} + \mathbf{C}_{\mathbf{RP}} \\ i\mathbf{C}^\dagger_{\mathrm{P}} & -i\mathbf{C}^{\mathrm{T}}_{\mathbf{P}} & \mathbf{I} + \mathbf{C}_{\mathbf{PR}} & \mathbf{C}_{\mathbf{PP}} \end{bmatrix} \begin{bmatrix} \dot{\mathrm{z}} \\ \dot{\mathbf{z}}^* \\ \dot{\mathbf{R}} \\ \dot{\mathbf{P}} \end{bmatrix} = \begin{bmatrix} \partial E/\partial \mathbf{z}^* \\ \partial E/\partial \mathbf{z} \\ \partial E/\partial \mathbf{R} \\ \partial E/\partial \mathbf{P} \end{bmatrix} \tag{8}$$

where the coupling elements in the dynamical metric are

$$(C_{XY})_{ij;kl} = -2\mathrm{Im}\left.\frac{\partial^2 \ln S}{\partial X_{ik}\partial Y_{jl}}\right|_{R'=R,P'=P} \tag{9}$$

$$(C_{X_{ik}})_{ph} = \left.\frac{\partial^2 \ln S}{\partial z^*_{ph}\partial X_{ik}}\right|_{R'=R,P'=P}, \quad C_{ph;qg} = \left.\frac{\partial^2 \ln S}{\partial z^*_{ph}\partial z_{qg}}\right|_{R=R',P'=P} \tag{10}$$

3. Free Electrons in Molecular Reaction Dynamics

In the simplest implementation of END, the electronic basis functions are centered on the average nuclear positions, which are dynamical variables. In the limit of classical nuclei these are the conventional basis functions used in molecular electronic structure theory. The electronic basis in END follows the dynamically changing nuclear positions. The evolution of the nuclear positions and momenta are governed by equations of motion that have the appearance of Newton's equations with the Hellmann−Feynman forces. The electronic dynamical variables are complex molecular orbital coefficients whose evolution is governed by the equations that are like those of the time-dependent Hartree−Fock (TDHF) approximation. The fact that the basis functions move with the dynamically changing nuclear positions introduces terms that couple the electronic and the nuclear dynamics. These coupling terms are the well-known nonadiabatic coupling terms. In the field of atomic collisions, such coupling terms are commonly eliminated by introducing so-called electron translation factors.

The principal idea in extending END to be able to treat free electrons (Note that the "free electrons" are indistinguishable and part of a fully antisymmetric wave function for all the system electrons.) as reactants and/or products is to center the basis on independent positions in space. This means that the basis function centers move on their own and are not associated with nuclear positions. This makes the positions $\mathbf{R}$ of these free centers dynamical variables with conjugate momenta $\mathbf{P}$, the evolution of which must be governed by the END equations. The derivation of these dynamical equations is quite straightforward using the time-dependent variational principle (TDVP). The free center basis consists of functions, very similar to those in eq 5, that can be expressed as

$$(x - R_x)^l (y - R_y)^m (z - R_z)^n \exp\left[-a(\mathbf{x} - \mathbf{R})^2 - \frac{i}{\hbar}\mathbf{P}\cdot(\mathbf{x} - \mathbf{R})\right] \tag{11}$$

with $\mathbf{x} = (x, y, z)$ an electron coordinate, $\mathbf{R}$ the center position, and $\mathbf{P}$ the average electronic momentum.

We first consider an END state vector with a single-determinant electronic description and distinguishable nuclei in the classical narrow wave packet limit. The system has N_{A} nuclei, N electrons, and the state vector is expressed in an electronic basis of rank K, the dynamical variables consist of the nuclear coordinates and momenta

$$\{\rho_{jk}, \pi_{jk}\}, \quad k = 1,2, ..., N_{\mathrm{A}}, \quad j = 1, 2, 3 \tag{12}$$

the coordinates and momenta of the centers of the basis functions that describe bound electrons (these centers are in a one-one correspondence to the nuclear average positions, but can evolve independently)

$$\{R_{jk},P_{jk}\}, \quad k = 1, 2, ..., N_{\mathrm{A}}, \quad j = 1, 2, 3 \tag{13}$$

the coordinates and momenta of the free centers of the electronic basis

$$\{R_{\mathrm{jf}}, P_{\mathrm{jf}}\}, \quad f = 1, 2, ..., N_{\mathrm{F}}, \quad j = 1, 2, 3 \tag{14}$$

and the Thouless molecular orbital coefficients

$$\{z_{\mathrm{ph}}\}, \quad h = 1, 2, ..., N; \quad p = N + 1, N + 2, ..., K \tag{15}$$

correspond to a partitioning of the spin−orbital basis ($\mathbf{u}^{\bullet}\ \mathbf{u}^{\circ}$), where the first part contains those spin−orbitals that are occupied and the second part those that are unoccupied in the reference determinantal wave function.

The choice of the number of free centers N_{F} is made so that it corresponds to the expected number of active electrons, i.e., for single ionization of a system in a collision with a structureless projectile such as a proton, one free center in the target is enough, while for, say, electron scattering one free center is assigned to the reagent free electron, and additional free centers may have to be chosen in the target system should the collision energy be such that ionization processes are likely, such as occur in (e,2e) spectroscopy.

The notations used are defined in reference 1, particularly section III.B. The metric matrix of the spin−orbital basis is

$$\Delta = \begin{pmatrix} \Delta^{\bullet} & \Delta^{>} \\ \Delta^{\vee} & \Delta^{\circ} \end{pmatrix} \tag{16}$$

The superscripts of the blocks in the matrix have the following meaning: The full "•" and empty "o" circles denote the occupied and unoccupied blocks. Because in general the occupied space is smaller than the unoccupied space, the upper-right off-diagonal block has the shape of a lying rectangle, hence the arrowlike superscript ">" pointing to the right. Similarly, the lower-left block is shaped like a tall rectangle as indicated by the arrowlike superscript "∨" pointing down. We use the intermediate compound variables

$$\mathbf{v} = -(\Delta^{\mathrm{V}} + \Delta^{\mathrm{o}}\mathbf{z})(\Delta^{\bullet} + \Delta^{>}\mathbf{z})^{-1} \tag{17}$$

which are elements of the $(K - N) \times N$ matrix. We also need the Fock matrix

$$\mathbf{F} = \mathbf{h} + \mathrm{Tr}(V_{ab;ab}\Gamma)_a \tag{18}$$

with the matrix $\mathbf{h}$ of single-particle integrals, which for electrons are

$$h_{ij} = \int u*_i(\mathbf{r})\left[-\frac{\hbar^2}{2m}\nabla^2 - \sum_{k=1}^{N_{\mathrm{A}}}\frac{Z_k e^2}{|\mathbf{r} - \mathbf{R}_k|^2}\right]u_j(\mathbf{r})\ \mathrm{d}^3r \tag{19}$$

and the matrix $\mathbf{V}$ of two-particle integrals

$$V_{ij;kl} = \langle ij|kl\rangle - \langle ij|lk\rangle \tag{20}$$

with

$$\langle ij|kl\rangle = \int\frac{u_i^*(\mathbf{r}_1)u_i^*(\mathbf{r}_2)u_k(\mathbf{r}_1)u_l(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\mathrm{d}^3r_1\mathrm{d}^3r_2 \tag{21}$$

for electrons and where the notation

$$\mathrm{Tr}(\mathbf{V}_{ab;ab}\Gamma)_a \equiv \sum_{i,j}V_{ik;jl}\Gamma_{ji} \tag{22}$$

is used. The single-particle density matrix is denoted Γ. The END equations become

$$i(\mathbf{v}\ \mathrm{I}^{\circ})\Delta\begin{pmatrix} 0 \\ \dot{\mathbf{z}} \end{pmatrix} + i(\mathbf{v}\ \mathbf{I}^{\circ})(\dot{\mathbf{R}}_l \cdot \nabla^{|\rangle}_{\mathbf{R}_l}\Delta + \dot{\mathbf{P}}_l \cdot \nabla^{|\rangle}_{\mathbf{P}_l}\Delta)\begin{pmatrix} \mathrm{I}^{\bullet} \\ \mathrm{z} \end{pmatrix} \tag{23}$$

$$= (\mathbf{v}\ \mathbf{I}^{\circ})\mathbf{F}\begin{pmatrix} \mathrm{I}^{\bullet} \\ \mathbf{z} \end{pmatrix}$$

$$\dot{\boldsymbol{\pi}}_k = -\nabla_{\boldsymbol{\rho}_k}E = \sum_{l\neq k}\frac{Z_k Z_l e^2(\boldsymbol{\rho}_k - \boldsymbol{\rho}_l)}{|\boldsymbol{\rho}_k - \boldsymbol{\rho}_l|^3} - \mathrm{Tr}(\nabla_{\boldsymbol{\rho}_k}h\Gamma) \tag{24}$$

$$\dot{\boldsymbol{\rho}}_k = \frac{\boldsymbol{\pi}_k}{M_k} \tag{25}$$

$$\sum_l[\mathbf{C}_{\mathbf{R}_k\mathbf{R}_l}\dot{\mathbf{R}}_l + \mathbf{C}_{\mathbf{R}_k\mathbf{P}_l}\dot{\mathbf{P}}_l] - 2\mathrm{ImTr}(\mathbf{C}^{\dagger}{}_{\mathbf{R}_k}\dot{\mathbf{z}}) =$$
$$\mathrm{Tr}(\nabla_{\mathbf{R}_k}\mathbf{h}\Gamma - \nabla_{\mathbf{R}_k}\Delta\Gamma\mathbf{h}\Gamma) +$$
$$\mathrm{Tr}\left[\mathrm{Tr}\left(\frac{1}{2}\nabla_{\mathbf{R}_k}V_{ab;ab}\Gamma - \nabla_{\mathbf{R}_k}\Delta\Gamma V_{ab;ab}\Gamma\right)_a\Gamma\right]_b \tag{26}$$

and

$$\sum_l[\mathbf{C}_{\mathbf{P}_k\mathbf{R}_l}\dot{\mathbf{R}}_l + \mathbf{C}_{\mathbf{P}_k\mathbf{P}_l}\dot{\mathbf{P}}_l] - 2\mathrm{ImTr}(\mathbf{C}^{\dagger}{}_{\mathbf{P}_k}\dot{\mathbf{z}}) =$$
$$\mathrm{Tr}(\nabla_{\mathbf{P}_k}\mathbf{h}\Gamma - \nabla_{\mathbf{P}_k}\Delta\Gamma\mathbf{h}\Gamma) +$$
$$\mathrm{Tr}\left[\mathrm{Tr}\left(\frac{1}{2}\nabla_{\mathbf{P}_k}V_{ab;ab}\Gamma - \nabla_{\mathbf{P}_k}\Delta\Gamma V_{ab;ab}\Gamma\right)_a\Gamma\right]_b \tag{27}$$

The electronic basis centered on the positions of atomic nuclei are standard bound state basis functions $\{u_i\}$, suitable for the particular element, while the electronic basis on a free center contains the union $\{w_i\} = \{u_i\} \cup \{v_i\}$ of the complete bound state basis and a diffuse set of functions $\{v_j\}$. To create an initial state, where the "free electron" is initially bound, one performs an SCF calculation for the system ground state (or possibly an excited state) in the bound state basis to obtain the SCF orbitals $\phi_i = \Sigma_k u_k c_{ki}$. Then the initial state component on a free center in a potential ionization process is formed using the projector $|w\rangle\langle w|w\rangle^{-1}\langle w|$ as

$$\bar{\phi}_k = \sum_{l,m}w_l(\Delta^{-1})_{lm}\langle w_m|\phi_k\rangle \tag{28}$$

In an electron scattering or recombination process the free center of the incoming electron has the functions $\{w_i\} = \{u_i\} \cup \{v_i\}$, where now the initial state of the free electron is some function v_i the width of which is chosen on the basis of the electron momentum and the time it takes the electron to arrive at the target. This has to be done in such a manner that the natural spreading of wave packets does not cause nonphysical behavior.

More flexible wave functions may be constructed. For instance, one may choose some, say N_{ion}, nuclei e.g. described as in eq 2 and with no electronic basis functions centered on them, and some, say N_{A}, nuclei with conventional electronic basis functions, and finally have some, say N_{F}, free centers with

TABLE 1: The Three Meaningful Combinations of Electronic Structure (single, SES, and multiple, MES) and Geometry (single, SG, and multiple, MG)

	SG	MG
SES	$\Psi\ (X, x, R, P)$	not meaningful
MES	$\Sigma_\mu\ c_\mu \Psi_\mu\ (X, R, P)$	$\Sigma_{\mu,\gamma}\ c_{\mu\gamma} \Psi_\mu\ (X, x, R_\gamma, P_\gamma)$

basis functions as in eq 11. In a particular molecular process some combination of these possibilities may be used.

4. General END Theory

Presentation of the possible realizations of END theory can be done with the aide of a four-dimensional table. Each of the four axes of this table lists two properties of the END wave function, such that

1. single (time-evolving) geometry (SG) versus multiple (time-evolving) geometries (MG),
2. single (time-evolving) electronic structure (SES) versus multiple (time-evolving) electronic structures (MES),
3. single-determinant wave function (SD) versus complete active space multiconfigurational wave function (CASMC), and
4. classical nuclei (CN) versus quantal nuclei (QN).

Of the possible $2^4 = 16$ entries in this table, only 12 cases are useful. One of these is the minimal implementation of single geometry, single electronic structure, single determinant, and classical nuclei. The terminology introduced in this table is given proper definition in the following.

4.1. Geometries. The term *geometry* is defined to mean a point in the generalized phase space for the total number of centers used to describe the END wave function. The notations R, P are used for the position and momenta vectors, such that

$$R = (\mathbf{R}_k, k = 1, ..., N_\mathrm{A} + N_\mathrm{F} + N_\mathrm{ion}) \tag{29}$$

where N_A is the number of atomic nuclei (centers of traditional electronic basis functions), N_F the number of free electron centers, and N_ion the number of nuclear centers with no basis functions attached. These coordinates can be classical positions and momenta when the nuclei are treated as classical particles, or average positions and momenta when they are treated as quantum particles.

4.2. Electronic Structures. We define an *electronic structure* to be an electronic wave function associated with a *geometry*. If the electronic structure is a single determinant, then multiple different electronic structures associated with the same geometry is a meaningful description. One can also conceive of multiple geometries each evolving independently with its own electronic structure. However, it is not meaningful to consider multiple geometries with a single electronic structure, because the Born−Oppenheimer approximation provides such a good description. Table 1 summarizes the combinations of geometry and electronic structure. The symbols X and x denote the quantum mechanical coordinates of the nuclei and the electrons, respectively. The index μ runs over electronic structures and γ over geometries.

4.3. Configurations. The choice of wave function to be used for the electronic structure can in principle be any of the constructions found in electronic structure theory. However, the choices used here are limited to wave functions that can be classified as single- and multiconfigurational, and for the latter only complete active space (CAS) wave functions are considered. The reason for this is that such wave functions have a well-established coherent state description, such that dynamics in terms of them can be constructed as a Hamiltonian system on a well-defined phase space. The single determinant is the Thouless coherent state[3,1] $|z, R, P\rangle$, and the CASMC wave function is the vector coherent state[32] $\Sigma_\kappa\, d_\kappa |z_\kappa, R, P\rangle$ (see section 5.1).

4.4. Nuclei. The molecular descriptions discussed above can all be employed with classical nuclei. Even if many processes can successfully be described with classical nuclei, it is sometimes necessary to use a fully quantal description of molecules and in the END framework it is clearly possible to do so.

One common choice of molecular wave function proceeds by a configuration interaction (CI), i.e. a superposition of orthogonal configurations approach, which leads to extremely long expansions and is therefore computationally not optimal. The END approach looks for more efficient parametrization than is provided by linear expansion coefficients. Nonlinear dependence on parameters is often a better choice. The success of the Born−Oppenheimer (BO) approximation and the clamped nuclei approximation implies that the classical nuclear coordinates are a good starting point for parametrization. In its simplest implementation END is derived as the narrow wave packet limit of frozen Gaussian wave packets for the nuclei. It can be seen from the dynamical equations, as was first pointed out by Heller,[23−27] that the structure of the equations is the same whether one takes the zero width limit or not. Only a slight renormalization of the matrix elements occurs, and the qualitative dynamics is the same.

END considers a basis for the nuclear orbitals centered at parametric positions R and with nuclear momentum factors, just like ETF's for electrons, with momentum P. These basis functions are denoted $|s, R, P\rangle$ for an s-type orbital (or a set of s-type orbitals), $|jk, R, P\rangle$ ($j = x, y, z$; $k = 1, 2, ..., N_\mathrm{A}$) for the p-type orbitals, $|jkil, R, P\rangle$ for the d-type orbitals, etc. It is now possible to define a fully quantal molecular wave function, similar to a Born−Huang series and corresponding to a single determinant for the electrons:

$$v|s, R, P\rangle|z, R, P\rangle + \sum_{j,k} v_{jk}|jk, R, P\rangle \frac{\partial}{\partial R_{jk}}|z, R, P\rangle + \sum_{j,k,i,l} v_{jkil}|jkil, R, P\rangle \frac{\partial^2}{\partial \mathrm{R}_{jk}\partial R_{il}}|z, R, P\rangle + ... \tag{30}$$

A Born−Huang series uses all electronic eigenstates instead of, as here, the derivatives of one electronic wave function. The electronic wave function $|z, R, P\rangle$ is not an eigenstate of the electronic Hamiltonian. The meaning of this *ansatz* is that it expresses a BO type correlation between electronic and nuclear motion. The first term is the simplest END wave function, where this correlation is expressed only through the parametric geometry of the basis function centers R and by P. The second term expresses that nuclear motion in the x, y, or z directions is correlated with specific changes in the electronic structure as described by an infinitesimal translation (derivative) along the respective Cartesian direction. To provide a more efficient notation for this type of wave functions a derivative operator,

$$\Xi_{l\omega} = \frac{\partial^l}{\partial R_{\omega_1} \cdots \partial R_{\omega_l}} \tag{31}$$

is introduced, where $\omega = (\omega_1, ... \omega_l) = (j_1k_1, ..., j_lk_l)$ is a l-tuple of Cartesian coordinate indices. The combination of electronic and nuclear wave function is shown in Table 2.

The three entries in Table 1 can now be combined with the four entries in Table 2 to show the full set of 12 possible END

TABLE 2: Single Determinantal Electronic Wavefunction (SD) or a CASMC Wavefunction Combined with Classical Nuclei (CN) or Quantum Nuclei (QN), Respectively

	CN	QN
SD	$\|R,P\rangle \|z, R, P\rangle$	$\Sigma_{l,\omega}\upsilon_{l\omega}\|l, \omega, R, \mathrm{P}\rangle\Xi_{l\omega}\|z, R, P\rangle$
CASMC	$\|R,P\rangle \Sigma_\kappa d_\kappa\|z_\kappa, R, P\rangle$	$\Sigma_{l,\omega,\kappa}\upsilon_{l\omega}d_\kappa\|l, \omega, \mathrm{R}, \mathrm{P}\rangle\Xi_{l\omega}\|z_\kappa, R, P\rangle$

TABLE 3: The Twelve Possible END Implementations Using Single (SG) or Multiple (MG) Geometry, Single (SES) or Multiple (MES) Electronic Structure, Classical (CN) or Quantum (QN) Nuclei, and the Associated Generalized Phase Spaces

type	geometry	electronic structure	configuration	nuclei	END phase space
1	SG	SES	SD	CN	R, P, z
2	SG	MES	SD	CN	$R, P, c_\mu, z_\mu,$
3	MG	MES	SD	CN	$R_\gamma, P_\gamma, c_{\mu\gamma}, z_{\mu\gamma}$
4	SG	SES	CASMC	CN	R, P, d_κ, z_κ
5	SG	MES	CASMC	CN	$R, P, c_\mu, d_{\kappa\mu}, z_{\kappa\mu},$
6	MG	MES	CASMC	CN	$R_\gamma, P_\gamma, c_{\mu\gamma}, d_{\kappa\mu\gamma}z_{\kappa\mu\gamma}$
7	SG	SES	SD	QN	$R, P, \upsilon_{l\omega}, z$
8	SG	MES	SD	QN	$R, P, \upsilon_{l\omega}, c_\mu, z_\mu$
9	MG	MES	SD	QN	$R_\gamma, P_\gamma, \upsilon_{l\omega\gamma}, c_{\mu\gamma}, z_{\mu\gamma}$
10	SG	SES	CASMC	QN	$R, P, \upsilon_{l\omega}, d_\kappa, z_\kappa$
11	SG	MES	CASMC	QN	$R, P, \upsilon_{l\omega}, c_\mu, d_{\kappa\mu}, z_{\kappa\mu}$
12	MG	MES	CASMC	QN	$R_\gamma, P_\gamma, \upsilon_{l\omega\gamma}, c_{\mu\gamma}, d_{\kappa\mu\gamma}, z_{\kappa\mu\gamma}$

implementations. From END type 1 through 12 one can discern an increasing flexibility, most of which is inspired by physical problems that may not be possible to describe satisfactorily with a wave function of simpler type. Furthermore, this hierarchy of types is designed to allow systematic improvements with incremental effort over the results obtained with classical nuclei. Type 2 wave functions introduce simple multiconfigurational structure making it possible to achieve proper spin multiplicity. Wave functions of type 3 permit the description of two or more open channels with nonnegligible probabilities. During, say, a reactive encounter the geometry R_1, P_1 initially evolves with a single determinant electronic description, then when a second channel becomes active two geometries may evolve to their respective final states, each with its own electronic structure. Types 4, 5, and 6 add the capability to base END on CASSCF quality electronic structure theory. CAS has been chosen because it allows a straightforward coherent state representation, which forms the foundation of END phase space dynamics.

The wave functions of types 7−12 duplicate types 1−6 but with full quantum mechanical description of the nuclei. The expansion in l for wave functions of type 7 is not expected to be used for high l values. Rather, it is being used to "flex out" a classical trajectory to exhibit the quantum mechanical quality. In applications that require the full range of quantum mechanical flexibility, for instance those where tunneling may be important, wave functions of type 9 or 12 should be used with a grid of geometries to cover configuration space completely and efficiently. Such calculations could probably be done with sufficient accuracy with expansions through $l = 2$.

5. Dynamical Equations

The dynamical equations for type 1 have been published and tested extensively in the program ENDyne[2] and are reviewed in section 2. Applications to numerous reactive collisions of ions, atoms, and molecules have been undertaken and published with, in general, good agreement with the best experiments for transition probabilities, differential, and total cross sections obtained with semiclassical corrections. The ENDyne code has been completely rewritten in Fortran 95 during the last year to allow the 11 other types to be implemented. Some of that effort is work in progress.

The dynamical equations can be derived following the same approach as for type 1[17] to obtain the Euler−Lagrange equations for all dynamical variables in the last column of Table 3. An explicit listing of these equations is far more complex than what is useful in this type of publication. Instead the general structure of the equations is presented and methods of solution discussed.

5.1. CASMC. In this section, the wave function of type 4 is discussed. The theoretical foundation for END in terms of a multiconfigurational electronic wave function using a complete active space (CASMC), sometimes referred to as CASSCF, has been introduced[32] in terms of an orthonormal basis and with a fixed nuclear framework. We extend this treatment here to a nonorthogonal basis of free centers with electron translation plane wave factors. The orbital space is divided into an occupied or hole space and an unoccupied or particle space. The hole space is further divided into a core space consisting of orbitals, which are present in all configurations and an active space, some of the orbitals of which may be occupied and some not in each configuration.

Let N be the number of electrons and K the rank of the spin−orbital basis. The core space, i.e. the spin−orbitals occupied in all determinants, has dimension K_1. We denote by K_2 the number of spin−orbitals that may be occupied in some determinant. This is the dimension of the hole space, while $K - K_2$ is the dimension of the particle space. The so-called active space of spin−orbitals has the dimension $K_2 - K_1$. Thus, we have that $0 \leq K_1 \leq N \leq K_2 \leq K$.

Neither are the occupied (core) orbitals and the active space orbitals necessarily orthogonal among themselves, nor to each other. However they are orthogonal to the unoccupied or particle space, whose orbitals also can be mutually nonorthogonal. This means that the CASMC electronic wave function considered here is an expansion in a set of nonorthogonal determinants

$$|d, z, R, P\rangle = \sum_\kappa d_\kappa |z_\kappa R, P\rangle \tag{32}$$

where $\kappa = (h_1, ..., h_N)$ is a comfiguration label with the indices $h_i \leq K_2$ in the hole space (core plus active space), and $|z_\kappa R, P\rangle$ is the determinant

$$\det \{\chi_{h_i}(\mathbf{x}_j)\} \tag{33}$$

with

$$\chi_{h_i} = u_{h_i} + \sum_{p=K_2+1}^{K} u_p z_{ph_i} = u_{h_i} + \sum_{p=K_2+1}^{K} u_p (z_\kappa)_{pi} \tag{34}$$

The total molecular wave function is chosen as $|\Psi(t)\rangle = |R(t),P(t)\rangle|d(t),z(t),R(t),P(t)\rangle$ (see eq 2), and the Lagrangian is calculated in the narrow nuclear wave packet limit. This leads to

$$\dot{\boldsymbol{\pi}}_k = \sum_{l \neq k} \frac{Z_k Z_l e^2 (\boldsymbol{\rho}_k - \boldsymbol{\rho}_l)}{|\boldsymbol{\rho}_k - \boldsymbol{\rho}_l|^3} - \mathrm{Tr}(\nabla_{\boldsymbol{\rho}_k} \mathbf{h}\Gamma)$$

$$\dot{\boldsymbol{\rho}}_k = \frac{\boldsymbol{\pi}_k}{M_k} \tag{35}$$

for the atomic nuclei without basis functions, and

$$\sum_l (\mathbf{C}_{\mathbf{R}_k\mathbf{R}_l}\dot{\mathbf{R}}_l + \mathrm{C}_{\mathbf{R}_k\mathbf{P}_l}\dot{\mathbf{P}}_l) + 2\mathrm{ImTr}(C^{\dagger}_{\mathbf{R}_k}\dot{\mathbf{z}}) + 2\mathrm{Im}\mathbf{D}^{\dagger}_{\mathbf{R}_k}\dot{\mathbf{d}}$$

$$= -\nabla_{\mathbf{R}_k}E$$

$$= \mathrm{Tr}(\nabla_{\mathbf{R}_k}\mathbf{h}\mathbf{\Gamma} - \sum_{K,K'} d^*_K \nabla_{\mathbf{R}_k}\Delta\Gamma_{KK'}d_{K'}) \tag{36}$$

$$- \mathrm{Tr}\left(\mathrm{Tr}\left(\frac{1}{2}\nabla_{\mathbf{R}_k}V_{ab;ab}\Gamma^{(2)} - \sum_{\kappa,\kappa'} d^*_\kappa \nabla_{\mathbf{R}_k}V_{ab;ab}\Gamma^{(2)}_{\kappa\kappa'}d_{\kappa'}\right)_a\right)_b$$

and an analogous equation for $\nabla_{\mathbf{P}_k}E$ for the atomic and free center degrees of freedom. In addition, the dynamical equations for the electronic parameters d and z given in ref 32 are to be added.

5.2. Multiple Geometries. In this section types 2, 3, 5, and 6 are discussed. Specifically two electronic structures with two geometries are considered and for clarity the P dependence is omitted. The END wave function, then, is

$$|\psi\rangle = |R_1\rangle|z_1, R_1\rangle + c|R_2\rangle|z_2, R_2\rangle \tag{37}$$

To avoid redundant unphysical dimensions in the parameter phase space the normalization is chosen such that the coefficient of the first term is unity. The global phase can be recovered (see ref 33). The dynamical variable expressing the configuration mixing is c. The dynamics may lead to regions of very large c values implying that the system state evolves to become purely $|R_2\rangle|z_2, R_2\rangle$. The differential equation solver in ENDyne automatically switches 1 and 2 so that the new c evolves to zero. As is the case for END type 1, the intent is to take the narrow wave packet limit for the nuclear part of the system wave function. However, a new issue now needs to be addressed concerning the behavior of the Lagrangian when the limit of zero widths ($b \rightarrow 0$, see eq 2) is taken for the case that the evolution goes to equal geometries ($R_1 = R_2$). The different scenarios are displayed in Table 4.

Let M be a diagonal matrix with nuclear masses, then write the END Lagrangian as

$$L = \frac{1}{2}[P_1\dot{R}_1 - R_1\dot{P}_1] - \frac{1}{2}M^{-1}P_1{}^2 + \frac{1}{2}[P_2\dot{R}_2 - R_2\dot{P}_2] - \frac{1}{2}M^{-1}P_2{}^2 + \langle\Psi|D_\mathrm{t} - H|\Psi\rangle/\langle\Psi|\Psi\rangle \tag{38}$$

with

$$D_\mathrm{t} = \frac{i}{2}\left[\frac{\mathrm{d}}{\mathrm{d}t} - \frac{\tilde{\mathrm{d}}}{\mathrm{d}t}\right] \tag{39}$$

and where the tilde means that the derivative is acting to the left. The overlap

$$S = \langle R_1|R_1\rangle\langle z_1, R_1|z_1, R_1\rangle + \langle R_2|R_2\rangle\langle z_2, R_2|z_2, R_2\rangle + c\langle R_1|R_2\rangle\langle z_1, R_1|z_2, R_2\rangle + c^*\langle R_2|R_1\rangle\langle z_2, R_2|z_1, R_1\rangle = G_1F_1 + G_2F_2 + cG_{12}F_{12} + c^*G^*_{12}F^*_{12} \tag{40}$$

is again an important quantity for the dynamical metric. An important part of the Lagrangian is

$$K = \langle\Psi|D_\mathrm{t} - H|\Psi\rangle = K_1 + K_2|c|^2 + \frac{i}{2}G_2F_2(c^*\dot{c} - c\dot{c}^*) + K_{12}c + \frac{i}{2}G_{12}F_{12}\dot{c} + K^*_{12}c^* - \frac{i}{2}\mathrm{G}^*_{12}\mathrm{F}^*_{12}\dot{c}^* \tag{41}$$

TABLE 4: The Behavior of the Lagrangian for the Relevant Cases of Differing Geometries and Nonzero Widths and the Limits to Equal Geometries and Zero Widths

width/geometry	$R_1 \neq R_2$	lim $R_1 \rightarrow R_2$	$R_1 = R_2$
$b_1, b_2 \neq 0$	$L_1 + L_2 + L_{12}$	continuous	$L_1 + L_2 + L_{12}$
$b_1 \rightarrow 0, b_2 \rightarrow 0$	continuous		continuous
$b_1 = b_2 = 0$	$L_1 + L_2$	$L_1 + L_2$	$L_1 + L_2 + L_{12}$

where

$$K_1 = \langle z_1, R_1|\langle R_1|D_\mathrm{t} - H|R_1\rangle|z_1, R_1\rangle \tag{42}$$

and so on. This means that the Lagrangian has the form

$$L = L_1 + L_2 + L_{12} \tag{43}$$

Observe that the limit of zero widths is not consistent with equal geometries. Because the nuclear wave functions are Gaussians, G_{12} is zero only at very large separations, and the only way the limits of zero widths and equal geometries can be made consistent is for $F_{12} = 0$. However, such a constraint is artificial within the END framework. The question is then to resolve this inconsistency in taking the limit of classical nuclei.

Throughout the development of END, one of the guiding principles in resolving apparent inconsistencies is to consider the full quantum mechanical expression. In this particular case the conclusion is that the widths of the nuclear wave packets must be kept finite in all expressions leading to the TDVP metric. For simplicity the widths are kept the same for all geometries. The situation is different for the Hamiltonian terms. Apart from a constant zero-point energy for each nuclear wave packet, the kinetic energy is the classical expression $^1/_2M^{-1}P^2$. The zero-point energy of Gaussian wave packets is not useful and is eliminated in the END calculations because it is just a constant energy shift. To account for zero-point vibrational energy effects in molecular reactions, a more flexible nuclear wave packet is required, as expressed by the wave functions of types 7−12. The true effects are related to differences in zero-point energies caused by changes in vibrational frequencies from one molecular state to another. Frozen Gaussians cannot describe such effects. The potential energy goes to the values for classical nuclei when the limit for zero widths is taken. It is computationally more efficient to use the values obtained with classical nuclei rather than to compute the nuclear expectation values for the Hamiltonian terms. The electronic expectation values are, of course, computed.

With the widths kept finite the physical content of the wave function in eq 37 is correct. The electronic structures evolve independently, when geometries are far apart, and interact when geometries are close.

With the expressions in eqs 38, 40, and 41, the Lagrangian can now be expressed as

$$L = \frac{1}{2}[P_1\dot{R}_1 - R_1\dot{P}_1] - \frac{1}{2}M^{-1}P_1{}^2 + K_1(z_1, R_1)/S + \frac{1}{2}[P_2\dot{R}_2 - R_2\dot{P}_2] - \frac{1}{2}M^{-1}P_1{}^2 + K_2(z_2, R_2)|c|^2/S + \frac{i}{2}[G_2F_2c^* + G_{12}F_{12}]\dot{c}/S - \frac{i}{2}[G_2F_2c + G^*_{12}F^*_{12}]\dot{c}^*/S + K_{12}c/S + K^*_{12}c^*/S. \tag{44}$$

As before the chain rule of differentiation can bring out the explicit dependence on the parameter velocities, such that

$$L = \frac{1}{2}[P_1 + Q_1]\dot{R}_1 + \frac{i}{2}[\omega_1^*\dot{z}_1 - \omega_1^*\dot{z}^*{}_1] + \frac{1}{2}[P_2 + Q_2]\dot{R}_2 + \frac{i}{2}[\omega_2^*\dot{z}_2 - \omega_2^*\dot{z}^*{}_2] + \frac{\mathrm{i}}{2}[a^*\dot{c} - a\dot{c}^*] - \frac{1}{2}M^{-1}P_1^2 - \frac{1}{2}M^{-1}P_2^2 - E \tag{45}$$

i.e., obviously referring to two coupled systems, where we have omitted the total derivative

$$\frac{\mathrm{d}}{\mathrm{d}t}[P_1R_1 + P_2R_2] \tag{46}$$

used to eliminate $\dot{P}$ and where

$$E = \langle\Psi|H_{\mathrm{el}}|\Psi\rangle/S \tag{47}$$

including the nuclear−nuclear repulsion energy. In analogy with the simplest END (type 1) approximation (see ref 17 and eq 6), the conjugate momenta to the z, R, and c dynamical variables are

$$\omega_1 = \frac{G_1}{S}\frac{\partial F_1}{\partial z_1^*} + \frac{G_{12}c}{S}\frac{\partial F_{12}}{\partial z_1^*}$$

$$\omega_2 = \frac{G_2}{S}\frac{\partial F_2}{\partial z_2^*} + \frac{G_{12}^*c^*}{S}\frac{\partial F_{12}^*}{\partial z_2^*} \tag{48}$$

$$P_1 + Q_1 = P_1 - \mathrm{Im}\left[\frac{G_1}{S}\frac{\partial F_1}{\partial R_1} + \frac{G_{12}c}{S}\frac{\partial F_{12}}{\partial R_1}\right]$$

$$P_2 + Q_2 = P_2 - \mathrm{Im}\left[\frac{G_2}{S}\frac{\partial F_2}{\partial R_2} + \frac{G_{12}^*c^*}{S}\frac{\partial F_{12}^*}{\partial R_2}\right] \tag{49}$$

and

$$a = [G_2F_2c + G_{12}^*F_{12}^*]/S \tag{50}$$

respectively.

The Euler−Lagrange eqs 7 for $q = z_1, z_2, R_1, R_2$, and c then yield the END dynamical equations. The structure of the END theory is such that all the ingredients of the equations for the type 1 wave function can be reused. The only additional feature being F_{12} and its derivatives. Because of the analyticity of $F_{12}(z_1^*, z_2)$, a property of the coherent state representation, it is a straightforward extension of $F_1(z_1^*. z_1)$. The overlap (eq 40) and the momenta depend on F_{12} yielding more complex expressions for the dynamical metric than is the case for type 1, but otherwise the structure of the dynamical equations is the same as for the simplest case.

This completes the analysis for the cases of multiple geometries and a single determinant for the electronic structures, i.e., types 1 and 2. The corresponding analysis for the CASMC types of electronic structures is completely analogous. The equations are, like those of higher order coupled cluster theory, better left to computer manipulations.

5.3. Quantum Nuclei. This section deals with wave function types 7−12. Because the END wave function with multiple geometries is already formulated with Gaussian wave packets, the extension to full quantum nuclei with the flexibility to employ arbitrary nuclear wave functions is fairly straightforward. The wave function in eq 30 is constructed from products of Gaussian type orbitals for the nuclear degrees of freedom and derivatives of electronic structure wave functions with respect to such degrees of freedom. For small systems it is often advantageous to use internal degrees of freedom, while for larger systems this is not that important. The geometry R for the wave function in eq 30 can be considered to be either laboratory or internal coordinates. The theory works for both cases. The structure of the Lagrangian for such a wave function is the same as that for the type 2 and 3 wave functions with the change that the nuclear and electronic parts have different forms instead of just depending on different sets of parameters.

Considering the expansion only through $l = 1$ the wave function can be expressed as

$$|\Psi\rangle = |R\rangle|z, R\rangle + \sum_k v_k|R_k\rangle\frac{\partial}{\partial R_k}|z, R\rangle \tag{51}$$

where again the normalization has been chosen such that the coefficient of the first term is 1 to avoid redundant dimensions in phase space. The Lagrangian now is simply

$$L = \langle\Psi|D_{\mathrm{t}} - H|\Psi\rangle/\langle\Psi/\Psi\rangle \tag{52}$$

and explicitly showing the time derivatives one can write

$$L = \frac{1}{2}Q\dot{R} + \frac{i}{2}[\omega^*\dot{z} - \omega\dot{z}^*] + \frac{i}{2}\sum_k[u_k^*\dot{v}_k - u_k\dot{v}_k^*] - E \tag{53}$$

with $E = \langle\Psi|H|\Psi\rangle/\langle\Psi/\Psi\rangle$, i.e., the full molecular expectation value including the nuclear kinetic energy terms. The conjugate momenta to the dynamical variables R, z, and v_k are

$$Q = -\mathrm{Im}\left[\frac{F}{S}\frac{\partial G}{\partial R} + \sum_k \frac{1}{S}\frac{\partial F}{\partial R_k}\frac{\partial G_k}{\partial R} + \frac{G}{S}\frac{\partial F}{\partial R} + \sum_k \frac{G_k}{S}\frac{\partial^2 F}{\partial z^*\partial R_k}\right] \tag{54}$$

$$\omega = \frac{G}{S}\frac{\partial F}{\partial z^*} + \sum_k \frac{G_k}{S}\frac{\partial F}{\partial R_k}$$

and

$$u_k = G_k\frac{\partial F}{\partial R_k}\,v_k \tag{55}$$

Here the definitions of F, G, and G_k should be evident from the analogy with the definitions in eq 40. The matrix elements required are higher derivatives of the kind that has been dealt with before.

Implementations of second-order derivatives already exists for the construction of dynamical equations with expansions through $l = 1$. The PRISM algorithm has been implemented to arbitrary order, which will allow the development of END with wave functions of type 7−12. Written in Fortran 95, it is structured to exploit both multithreading shared memory and MPI distributed memory parallelism. It has been designed both as an extension to Tcl and Python and has both Tcl and Python imbedded in it. This has been done with the aim to allow more flexibility in using advanced features (extension) and to support rapid prototyping of the complex wave functions discussed in this paper (embedding). The redesigned ENDyne version 5 is now nearly complete.

6. Conclusion

The complete design ideas of the END theory and our vision for its implementation have been discussed in some detail. It should be clear from this discussion that END provides a smooth, practical, and efficient hierarchy of descriptions of molecular processes, that ranges from classical nuclei with a single END determinant for the electrons to a full quantum mechanical description with CASMC wave functions for the electrons.

Acknowledgment. The support of National Science Foundation through Grant CHE-9732902 and the Office of Naval Research through Grant N0014-97-1-0261 are gratefully acknowledged. The interaction and collaboration with Denis Jacquemin, Remigio Cabrera-Trujillo, and other members of our research group has been an inspiration for this work.

References and Notes

(1) Deumens, E.; Diz, A.; Longo, R.; Öhrn, Y. *Rev. Mod. Phys* **1994**, *66*, 917.

(2) E. Deumens et al. *ENDyne Software for Electron Nuclear Dynamics*; Quantum Theory Project: University of Florida, Gainesville, FL 32611-8435, 1996.

(3) Thouless, D. J. *Nucl. Phys.* **1960**, *21*, 225.

(4) Deumens, E.; Öhrn, Y. *J. Phys. Chem.* **1988**, *92*, 3181.

(5) Deumens, E.; Öhrn, Y. *Int. J. Quantum Chem.*: *Quantum Chem. Symp.* **1989**, *23*, 31.

(6) Deumens, E.; Öhrn, Y. *J. Mol. Struct.* (*THEOCHEM*) **1989**, *199*, 23.

(7) Öhrn, Y.; et al. Time Evolution of Electrons and Nuclei in Molecular Systems. In *Time-Dependent Quantum Molecular Dynamics*; Broeckhove, J., Lathouwers, L., Eds.; Plenum: New York, 1992; pp 279−292.

(8) Deumens, E.; Diz, A.; Taylor, H.; Öhrn, Y. *J. Chem. Phys.* **1992**, *96*, 6820.

(9) Öhrn, Y.; Deumens, E. Electron Nuclear Dynamics with Coherent States. In *Proceedings of the international Symposium on Coherent States: Past, Present, and Future*; Feng, D. H., Klauder, J. R., Eds.; Oak Ridge Associated Universities, World Scientific: Singapore, 1993.

(10) Longo, R.; Deumens, E.; Öhrn, Y. *J. Chem. Phys.* **1993**, *99*, 4554.

(11) Longo, R.; Diz, A.; Deumens, E.; Öhrn, Y. *Chem. Phys. Lett.* **1994**, *220*, 305.

(12) Diz, A.; Öhrn, Y.; Sabin, J. R. *Nucl. Instrum. Methods B* **1995**, *B96*, 633.

(13) Morales, J. A.; Diz, A. C.; Deumens, E.; Öhrn, Y. *Chem. Phys. Lett.* **1995**, *233*, 392.

(14) Morales, J. A.; Diz, A. C.; Deumens, E.; Öhrn, Y. *J. Chem. Phys.* **1995**, *103*, 9968.

(15) Öhrn, Y.; Oreiro, J.; Deumens, E. *Int. J. Quantum Chem.* **1996**, *58*, 583.

(16) Jacquemin, D.; Morales, J. A.; Deumens, E.; Öhrn, Y. *J. Chem. Phys.* **1997**, *107*, 6146.

(17) Deumens, E.; Öhrn, Y. *J. Chem. Soc.*, *Faraday Trans.* **1997**, *93*, 919.

(18) Hedström, M.; Morales, J. A.; Deumens, E.; Öhrn, Y. *Chem. Phys. Lett.* **1997**, *279*, 241.

(19) Hedström, M.; Deumens, E.; Öhrn, Y. *Phys. Rev. A* **1998**, *57*, 2625.

(20) Cabrera-Trujillo, R.; Sabin, J. R.; Öhrn, Y.; Deumens, E. *Phys. Rev. Lett.* **2000**, *84*, 5300.

(21) Cabrera-Trujillo, R.; Öhrn, Y.; Deumens, E.; Sabin, J. R. *Phys. Rev. A* **2000**, *62*, 052714 1.

(22) Klauder, J. R.; Skagerstam, B.-S. *Coherent States*, *Applications in Physics and Mathematical Physics*; World Scientific: Singapore, 1985.

(23) Heller, E. J. *J. Chem. Phys.* **1975**, *62*, 1544.

(24) Heller, E. J. *Chem. Phys. Lett.* **1975**, *34*, 321.

(25) Heller, E. J. *J. Chem. Phys.* **1976**, *65*, 4979.

(26) Heller, E. J. *J. Chem. Phys.* **1977**, *66*, 5777.

(27) Heller, E. J. *Acc. Chem. Res.* **1981**, *14*, 386.

(28) Weiner, B.; Deumens, E.; Öhrn, Y. *J. Math. Phys.* **1994**, *35*, 1139.

(29) Manthe, U.; Köppel, H.; Cederbaum, L. S. *J. Chem. Phys.* **1991**, *95*, 1708.

(30) Köppel, H.; Manthe, U. Femtosecond Wave Packet Dynamics on Strongly Coupled Potential Energy Surfaces. In *Time Dependent Quantum Molecular Dynamics*; Broeckhove, J., Lathouwers, L., Eds.; Plenum Press: New York, 1992; pp 83−95,

(31) Manthe, U.; Meyer, H.; Cederbaum, L. S. *J. Chem. Phys.* **1992**, *97*, 3199.

(32) Deumens, E.; Öhrn, Y.; Weiner, B. *J. Math. Phys.* **1991**, *32*, 1166.

(33) Löwdin, P.-O.; Mukherjee, P. K. *Chem. Phys. Lett.* **1972**, *14*, 1.