Time-dependent theoretical treatments of the dynamics of electrons and nuclei in molecular systems

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An overview is presented of methods for time-dependent treatments of molecules as systems of electrons and nuclei. The theoretical details of these methods are reviewed and contrasted in the light of a recently developed time-dependent method called electron-nuclear dynamics. Electron-nuclear dynamics (END) is a formulation of the complete dynamics of electrons and nuclei of a molecular system that eliminates the necessity of constructing potential-energy surfaces. Because of its general formulation, it encompasses many aspects found in other formulations and can serve as a didactic device for clarifying many of the principles and approximations relevant in time-dependent treatments of molecular systems. The END equations are derived from the time-dependent variational principle applied to a chosen family of efficiently parametrized approximate state vectors. A detailed analysis of the END equations is given for the case of a single-determinantal state for the electrons and a classical treatment of the nuclei. The approach leads to a simple formulation of the fully nonlinear time-dependent Hartree-Fock theory including nuclear dynamics. The nonlinear END equations with the *ab initio* Coulomb Hamiltonian have been implemented at this level of theory in a computer program, ENDyne, and have been shown feasible for the study of small molecular systems. Implementation of the Austin Model 1 semiempirical Hamiltonian is discussed as a route to large molecular systems. The linearized END equations at this level of theory are shown to lead to the random-phase approximation for the coupled system of electrons and nuclei. The qualitative features of the general nonlinear solution are analyzed using the results of the linearized equations as a first approximation. Some specific applications of END are presented, and the comparison with experiment and other theoretical approaches is discussed.

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I. INTRODUCTION

Dynamics of molecular systems has been of interest in chemical physics and physical chemistry since the advent of quantum mechanics. Over the years many theoretical approaches have been formulated and implemented in detail. Computational methods for efficient solution of the resulting equations have been devised in many cases. Although the basic equation of quantum mechanics is a time-dependent equation, in the Schrödinger, Heisenberg, or interaction representation, the fact that separation of variables is possible and the intractability of the equation for systems of any complexity have led to a situation in which several generations of scientists have been trained to focus on the time-independent equation both for bound-state and for scattering problems. In the last decade, however, the time-dependent formulation has attracted more attention. It has become clear that solving the time-dependent equation directly is indeed possible and sometimes computationally advantageous over first finding all relevant stationary-state eigenfunctions for a given problem.

Time-dependent descriptions have always appealed to researchers' intuition, as evidenced by the fact that experiments are often discussed, both by experimenters and by theorists, in a time-dependent language. One of the more dramatic situations in this respect is provided by the field of femtosecond spectroscopy (Zewail and Bernstein, 1988; Zewail, 1989) where the time evolution of nuclei and electrons in molecular systems can be followed in detail. In the last decade, time-dependent theoretical treatments have matured to the extent that detailed theoretical descriptions matching experimental accomplishments are feasible. Another indicator of the growing importance of time-dependent descriptions is the discovery, in the theory of measurement, that histories of events as the basic concept, rather than the events themselves, lead to a consistent interpretation of quantum mechanics. In an important review, Omnès (1992) shows that consideration of consistent sequences of properties in time is an essential ingredient and allows the Copenhagen Interpretation to be extended to a consistent interpretation of quantum mechanics. It is too early to state that these developments will end the long debate on the interpretation of quantum mechanics; but it is notable that explicit consideration of time is put forth as a key element in that long debate, and that its introduction actually strengthens and simplifies the original Copenhagen Interpretation.

The aims of this paper are (1) to review the most prominent of the time-dependent methods, analyzing and comparing the principles and approximations underlying them as well as commenting on their computational implementation; (2) to present most of these methods and techniques from a general, unified, and didactic point of view, which is provided by the time-dependent variational principle; and (3) to outline in considerable detail one method—electron-nuclear dynamics (END)—that is a rigorous application of the time-dependent variational principle and is therefore a useful framework for explaining the differences between various methods. The main emphasis is on time-dependent methods; but because potential-energy surfaces play such an important role in the theory of molecular phenomena, some attention is paid to the construction of approximations to eigenstates of the electronic Hamiltonian. However, no attempt is made to review the field of electronic structure theory. Only those methods are mentioned that in some way can be considered as special cases of time-dependent methods.

Although we try to give a fair account of the state of the field, our review is biased by our own experiences and is not intended to be exhaustive. We apologize for any omissions.

Atomic units will be used throughout this work; i.e., $\hbar=1$, $m_e=1$, and $e=1$.

A. Plan of presentation

To present an overview of the many theoretical methods of time-dependent treatments of molecular processes, (i) the time-dependent variational principle and (ii) the concept of potential-energy surfaces are used.

The time-dependent variational principle (TDVP), when the trial wave function is completely general and not restricted in any form, yields the time-dependent Schrödinger equation (Dirac, 1930), as shown in Sec. II.D. On the other hand, any choice of a restricted form of trial function in the TDVP results in time-dependent equations that approximate the Schrödinger equation. Based on this, one can discern three different classes of methods. First, the time-dependent Schrödinger equation (in principle obtained from the completely unrestricted TDVP) can be studied and approximate solutions found to obtain transition amplitudes and spectral information in a variety of ways. Second, a separation of variables yields the time-independent Schrödinger equation, which can be studied to find approximate stationary-state solutions. The third class of methods are those, as stated above, that directly restrict the TDVP trial function and obtain dynamical equations that approximate the time-dependent Schrödinger equation.

Alternative variational principles known as the Dirac-Frenkel variational principle (Dirac, 1930; Frenkel, 1934) and the McLachlan variational principle (McLachlan and Ball, 1964) are equivalent to the TDVP as long as complex wave functions analytic in the parameters are used and the global phase of the wave function is retained (Kučar *et al.*, 1987; Broeckhove *et al.*, 1988).

Earlier theoretical work related to the general approach of this review is that of Kerman and Koonin (1976), who first showed that the TDVP applied to a parametrized family of wave functions leads to a classical Hamiltonian system of equations for the parameters. Rowe and Basserman (1976) later introduced the theory of coherent states to provide a general framework for parametrized wave functions, and Kramer and Saraceno (1981) worked out the geometry of the TDVP.

Treatments of molecular systems often use the concept of potential-energy surface obtained (at least in principle) from solving the time-independent Schrödinger equation with the electronic Hamiltonian for a large number of fixed nuclear geometries. The widely used concept of a potential-energy surface can serve to distinguish between different approaches, in that it summarizes how the electronic subsystem is treated.

Methods that use a single potential-energy surface adhere to the Born-Oppenheimer approximation, or the

TABLE I. Overview of theoretical molecular methods classified by the use of potential-energy surface and time dependence. The nature of the treatment of the nuclei is indicated as classical, semiclassical, and quantum mechanical.

PES	Nuclei	Time independent	Time dependent
Single	Classical	Energetics, equilibrium geometries, transition states, barrier heights, reaction paths	Molecular dynamics using model forces or the gradient of a fitted or directly computed PES (Carmer *et al.*, 1993)
	Semiclassical	Reaction rates from transition-state theory (Melissas *et al.*, 1992)	Semiclassical molecular dynamics, time correlation functions in eikonal approximation (Micha and Villalonga, 1993), wave-packet dynamics (Huber *et al.*, 1988)
	Quantum	Vibrational and rotational eigenstates (Lathouwers *et al.*, 1987), multichannel scattering and reactive collisions with or without constrained geometries, (variational) *R*-matrix (Linderberg *et al.*, 1989) and *S*-matrix (Miller and op de Haar, 1987) approaches, method of perturbed stationary states (Mott and Massey, 1965; Riera, 1992)	Quantum molecular dynamics with representation on a grid of points or with a set of basis functions (Feit and Fleck, 1980; Kosloff and Kosloff, 1983a; Tal-Ezer and Kosloff, 1984; Leforestier *et al.*, 1991; Manthe *et al.*, 1992b), single and multiconfiguration time-dependent self-consistent field (Manthe *et al.*, 1992a)
Multiple	Classical		Surface hopping model (Tully and Preston, 1971)
	Semiclassical		
	Quantum	Reactive processes and calculation of nonadiabatic couplings (Lengfield and Yarkony, 1992)	Wave-packet dynamics on vibronically coupled surfaces (Coalson, 1989; Manthe *et al.*, 1991)
Not used	Classical		Time-dependent Hartree-Fock (Dirac, 1930)
	Semiclassical		Car-Parrinello (1985), electron-nuclear dynamics (Deumens, Diz, Taylor, and Öhrn, 1992), close-coupling methods (Delos, 1981)
	Quantum	Diagonalization in a basis of electronic and vibrational states (Kolos and Wolniewicz, 1964), many-body scattering calculations as basis for molecular structure calculations (Levin, 1978) and for molecular reactions (Micha, 1985)	Perturbed-stationary-states and close-coupling methods (Delos, 1981)

adiabatic approximation if the diagonal correction term to the nuclear kinetic energy $\langle \varphi(R)|\Delta_R|\varphi(R)\rangle$ is included in the potential-energy surface. The description of the electrons is, in this case, limited to the single eigenstate associated with the potential-energy surface; e.g., they cannot have any momentum expectation value, since the electronic eigenfunctions $\varphi(r,R)$ are always real. A second group of methods employs several potential-energy surfaces, most often two, and includes the nonadiabatic correction terms. Because several electronic eigenstates, in principle a complete set, are involved, an accurate description of the electrons is possible. A third group avoids the construction of intermediate electronic eigenstates and describes the electrons in some other way.

In order to use a potential-energy surface as a potential energy for the nuclear dynamics, its discrete representation is usually fitted (interpolated) with some analytical representation. Such procedures are generally difficult and may introduce errors that are hard to control. The concept of a potential-energy surface traditionally plays an important role in the interpretation of spectra and is often also considered convenient for discussing dynamical processes even when several surfaces have to be employed. The importance placed on the existence of potential-energy surfaces, however, is somewhat limiting in that high-quality potential-energy surfaces can be obtained, so far, only for the low-lying states of simple systems.

With these principles a rough classification of the field of molecular theory is obtained which is presented in Table I.

In this review, time-independent methods are not treated at all, with the exception of those methods that follow naturally from a time-dependent treatment by setting the time derivatives equal to zero, as, for example, in Sec. III.C. This review deals in detail only with time-dependent methods that do not use potential-energy surfaces. Other approaches are discussed incompletely for comparison in Sec. I.B.

In Sec. II the details of the physical and mathematical aspects of the basic ingredients are discussed for several time-dependent treatments. Such details include the electronic orbitals, which are fundamental to the description of the electrons and constitute the ingredients of the electronic wave functions used for the calculation of the potential-energy surface. The form of the electronic orbitals is also important for the explicit treatment of the electron dynamics. Comments are made on treatments of the nuclear dynamics, and the time-dependent variational principle is introduced.

In Sec. III a rigorous and detailed treatment of the simultaneous dynamics of electrons and nuclei is presented. During this derivation, the opportunity arises to discuss how various choices lead to each of the most prominent of the time-dependent treatments. Both *ab initio* and semiempirical molecular Hamiltonians are treated, as are the theoretical and computational implications of various assumptions for the dynamical equations. The structure of the dynamical equations of the END is compared to that of the equations obtained through other methods, in particular the close-coupling approach. Linearization of the dynamical equations is analyzed to reveal the general structure of the solution. This leads to the random-phase-approximation equations for coupled electrons and nuclei. This is recognized as a scheme used in several theoretical approaches to deal with the different time scales of electronic and nuclear evolutions.

In Sec. IV some applications of END to collision problems are treated involving some one- and two-electron systems (ion-atom and ion-molecule collisions). An intramolecular electron-transfer problem for a simple model system is used to illustrate how the END theory is applied to such cases.

Section V, with a discussion of the methods with regard to physical principles such as conservation laws and time reversal, concludes this review.

Detailed working expressions for the END approach are given in terms of both molecular and atomic spin-orbitals using a single determinant for the electrons and a classical treatment of the nuclei in Secs. 1 and 2 in the Appendix. A brief definition of semiempirical Hamiltonians can be found in Sec. 3 in the Appendix.

B. Overview of methods

Recent years have seen increased efforts in the development and application of explicitly time-dependent methods to a great variety of chemical and physical problems on the molecular level. A brief overview is presented of this activity in the last decade. This work has intensified dramatically in the last five years, stimulated both by the advent of high-accuracy time-resolved experiments and the realization that a time-dependent description can offer valuable insights and accurate descriptions of many processes.

The time-dependent methods are based on many different levels of theory. Some have a phenomenological basis, like the method of Car and Parrinello (1985) which was recently reviewed by Remler and Madden (1990). Other methods are derived from a variational principle, such as the time-dependent Hartree-Fock, or are exact solutions to the Schrödinger equation, such as the numerical wave-packet propagation. Some techniques can only provide qualitative insight into the time evolution, while others provide accurate, predictive values for such physical properties as scattering cross sections and transition probabilities. Some methods require modest computational efforts and can be applied to quite general systems, while others are so computationally demanding that only problems reducible to three degrees of freedom or less are currently amenable to calculations.

1. Potential-energy surfaces

The study of molecular systems has traditionally proceeded by solving the electronic problem first to obtain a molecular potential-energy surface (PES) with an associated electronic eigenstate. The methods of construction of reliable PES's constitute an extensive field of study (see, e.g., the review by Dunning and Harding, 1985, for *ab initio* surfaces and the review by Kuntz, 1985, for semiempirical ones). The dynamics of the molecule is then reduced to the dynamics of the nuclei on that PES, at the classical, semiclassical, or quantum level. This approach raises the following issues that are addressed in different ways by the various methods.

(1) Construction of the electronic eigenstates for one geometry is a nontrivial problem in itself. In order to obtain a useful representation of the surface for all geometries needed for the relevant dynamics, one must resort to solving the electronic problem at selected geometries and perform an interpolation or fit using a suitable analytic form for the surface to define its value at other geometries.

(2) The process of constructing a faithful fit is also a sizable task. Usually different analytic forms are needed for different regions. And it has been found (Liu and Murrell, 1991; Aguado and Paniagua, 1992) that small errors in curvature of the fit can produce significantly different dynamics. Accurate fits are available for some triatomic systems and for a few four-atom molecules. It is generally believed that fits for general polyatomic systems will be hard to come by.

(3) An electronic state associated with a PES is completely static. The errors introduced in the molecular dynamics are usually neglected by investigators looking for low-energy and adiabatic rearrangement reactions and infrared spectroscopy. However, for other situations, such as charge-transfer reaction studies, some of the errors cannot be neglected. To overcome that limitation, methods such as perturbed stationary states use multiple PES's, and close-coupling or time-dependent Hartree-Fock methods use electron translation factors (ETF's).

The methods that rely on a single or multiple PES assume that a surface is given in a numerically accessible form. Sometimes this is accomplished with a global fit or patches of local spline fits to a set of points obtained from accurate electronic structure calculations. The best methods for global surfaces are electronic multiconfigurational self-consistent-field calculations (Olsen *et al.*, 1983; Jensen and Ågren, 1986). Full configuration interaction with a realistic basis is, of course, feasible only for the smallest systems. A systematic procedure for generating model potential-energy surfaces for general molecules is that of diatomics in molecules, with *ab initio* and semiempirical implementations (Dunning and Harding, 1985).

Methods for constructing the PES at the sampling points, which usually include critical points like local minima, saddle points, and reaction paths, are not covered by this review; neither are the techniques of interpolation of PES data points. However, some of the time-dependent methods, which do not rely on the PES, possess a natural time-independent special case that can effectively be used to find eigenstates to the electronic Hamiltonian and, thus, to construct PES's (see Sec. III.C).

2. Quantum dynamics on a single surface

There is a growing literature of methods that can be referred to as "direct approaches." Such numerical methods have two key features. One is the representation of the wave function, either by expansion coefficients in a basis set or by discretization on a grid of points. This, in turn, determines how to evaluate the action of the operators, in particular, the Hamiltonian $\hat{H}=\hat{K}+\hat{V}$ with its kinetic-energy operator $\hat{K}$ and its potential-energy operator $\hat{V}$, on the wave function. The other feature is the actual time propagation algorithm, i.e., how the solution is marched over a time interval, given its value at the initial time.

a. Exact wave-packet propagation

It is possible to solve exactly the Schrödinger equation for the internal degrees of freedom of molecules with three or four atoms by representing the wave function on a numerical grid. These methods are known as the discrete variable representation and the pseudospectral approximation, depending on whether one prefers to stress the numerical representation or the method of solution. The pseudospectral Fourier approximation (Gottlieb and Orszag, 1977) was introduced rather recently into molecular dynamics, although for some time it had been used in several areas of physics, for example, fluid dynamics, optics, and electron microscopy. This approach employs a grid representation of the wave function in coordinate space and applies the discrete Fourier transform to obtain a momentum space representation. Computer codes performing fast Fourier transform are generally available, making it possible to switch from coordinate space to momentum space and back so as to allow for fast evaluation of the action of the kinetic-energy and the potential-energy terms of the Hamiltonian. Error analysis and collocating functions other than plane waves are available within this technique. Appropriate functions for radial (Bisseling and Kosloff, 1985) and angular coordinates (Quéré and Leforestier, 1990) have been implemented.

There are various time integration algorithms currently in use with the pseudospectral method in molecular dynamics. One can distinguish four, namely, the second-order-difference method, the split-operator method, the short-time iterative Lanczos method, and the Chebyshev expansion method.

When the second-order difference (Kosloff and Kosloff, 1983a) is applied to the Schrödinger equation, the wave function is computed at successive short time steps through a combination of a forward and a backward move, which eliminates the second-order terms; so the error is of third order in the time step. The other three methods focus on the propagator. In the split-operator scheme (Feit and Fleck, 1980), one makes a symmetric decomposition of the exact propagator

$$\begin{aligned} &\hat{U}(\epsilon)=\exp(-i\hat{H}\epsilon) , \\ &\psi(\epsilon)=\hat{U}(\epsilon)\psi(0) , \qquad (1.1)\\ &\hat{U}(\epsilon)\approx\exp\left[-i\frac{\epsilon}{2}\hat{K}\right]\exp(-i\epsilon\hat{V})\exp\left[-i\frac{\epsilon}{2}\hat{K}\right] , \end{aligned}$$

introducing a third-order error term. This is a short-time method that requires successive applications to propagate over a finite time interval.

The short-time iterative Lanczos propagation formula (Leforestier *et al.*, 1991) is

$$U(\epsilon)\approx\exp[-i\epsilon\Lambda(\hat{H},\psi(0))] , \qquad (1.2)$$

where U is now a matrix operator in the Krylov subspace generated by the Hamiltonian and the initial wave function. The matrix Λ is the tridiagonal Lanczos matrix representing the Hamiltonian in the Krylov space (Cullum and Willoughby, 1985). The exponentiation is usually performed by diagonalizing the Lanczos matrix and working with the diagonal eigenvalue matrix. The length of time dictates the size of the Krylov space needed for a predefined accuracy (Park and Light, 1986). In general, short time steps are used in order not to lose the advantage of the Lanczos reduction; i.e., iterating the algorithm is more efficient than using long time steps.

The Chebyshev expansion method (Tal-Ezer and Kosloff, 1984) approximates the exact propagator by a Chebyshev expansion,

$$\hat{U}(t)=\sum_{n=1}^{N} a_n(t)T_n(-i\hat{H}_R) , \qquad (1.3)$$

where the Hamiltonian needs to be renormalized so that its spectrum coincides with the domain of the Chebyshev polynomials T_n. This is a long-time method. The convergence requirement on the Chebyshev expansion is such that the number of terms does not decrease significantly for smaller t values. Thus, for efficiency, t should be large.

Should one want to consider time-dependent Hamiltonians, there are straightforward ways to extend the split-operator, second-order-difference, and short-time iterative Lanczos methods to such cases, while the Chebyshev expansion method would seem not to have this flexibility. For short-time methods, further approximations are usually implied, such as the use of short-time averaged Hamiltonians and the disregard of time ordering.

The specific merits of various methods to evaluate the action of the Hamiltonian on the wave function and to propagate the solution in time have been reviewed by Kosloff (1988). The computational effort involved in these methods is presently such that applications involving at most a few degrees of freedom can be attempted. They are used to study quantum dynamics of nuclear motion on a potential-energy surface or on a small number of coupled potential-energy surfaces. The split operator offers limited accuracy and has been used in studies of reactions (Kosloff and Kosloff, 1983b) and absorption spectra (Tang *et al.*, 1990). The second-order difference has been used extensively because of its ease of implementation of eigenspectra (Feit *et al.*, 1982), nonadiabatically coupled systems (Alvarellos and Metiu, 1988; Manthe and Köppel, 1990b), dissociation and predissociation processes (Manthe *et al.*, 1991), photodetachment spectra (Engel, 1991), and systems with time-dependent Hamiltonians (Cheslowski *et al.*, 1990). A significant number of applications of the Chebyshev expansion method have been made, among other problems, to atom-diatom collisions (Sun *et al.*, 1987), to a multiconfigurational self-consistent-field approach (Hammerich *et al.*, 1990), to photodissociation (Kulander *et al.*, 1991), and to the computation of energy levels (Kosloff and Tal-Ezer, 1986; Neuhauser, 1990).

b. Time-dependent self-consistent field

This method explored by Kossloff and Ratner (Bisseling *et al.*, 1987), among others, reduces the many variable Schrödinger equations for the nuclei to a set of coupled equations for each nuclear coordinate moving in the average field of the others. Wave packets are represented on a grid and are products of packets, each in one interval coordinate only. Since a single configuration state cannot properly describe the division of probability over two channels, the method was extended to allow for multiconfigurational states. This permits a proper description of reactions where two exit channels are populated. The method is also known as the time-dependent Hartree approximation. A variation on the method, called time-dependent rotated Hartree, was developed by Meyer and co-workers (Meyer *et al.*, 1988).

3. Trajectories on a single surface

a. Fitted surface

Molecular dynamics as the Newtonian mechanics of nuclei with effective two-, three-, and four-body forces has been used with great success to study many molecular processes. For large molecules this is still the only practical method, and it is in general use, especially in organic chemistry and biochemistry. It is used to investigate reactions and to explore molecular geometries. Often the dynamics is used as an efficient means to search for minima of energy rather than to reveal time-dependent effects.

Molecular dynamics on fitted surfaces is also used to compute reaction rates using classical statistical methods. Sometimes the trajectories are used in a semiclassical formulation to obtain quantum-mechanical approximations.

The so-called eikonal approximation (Mott and Massey, 1965) derives classical equations for nuclear positions and momenta.

One semiclassical scheme is the wave-packet dynamics of Heller (Huber and Heller, 1987). It is derived via the time-dependent variational principle (TDVP) by considering all translated and Galilei-boosted Gaussian wave packets for the nuclear coordinates as the manifold of allowed wave functions. Requiring that the action be stationary then yields the familiar Euler-Lagrange equations. For translated and Galilei-boosted Gaussian wave packets, these correspond to classical Hamiltonian equations for the variables R and P, which are the average nuclear positions and momenta in the Gaussian wave packets. The method can be easily extended to include a scaling parameter, resulting in so-called thawed, as opposed to frozen, Gaussians. The applications with this additional degree of freedom require careful interpretation, as their results are sometimes misleading (Reimers and Heller, 1988).

The wave-packet dynamics method has been extended, by enlarging the set of allowed wave functions in the TDVP, to describe more complex wave packets constructed as superpositions of time-dependent basis functions (Kučar and Meyer, 1989).

With time correlation functions these methods can yield transition probabilities (Villalonga and Micha, 1992).

b. Computed surface

An increasing number of workers need more accessible surfaces then those fitted from electronic structure calculations in order to study intermediate-size systems. Molecular dynamics using gradients from a semiempirical Hamiltonian has been implemented by Stewart in MOPAC (Stewart, 1990), by Dewar in AMPAC (Dewar *et al.*, 1985), and by Weiner (Carmer *et al.*, 1993; Zhao *et al.*, 1993) and independently by Edwards (1992) in ZINDO (Zerner, 1991). These researchers have implemented Newtonian molecular-dynamics methods using directly calculated gradients in semiempirical electronic structure codes. This allows efficient time-dependent studies of dynamics on a single surface. The forces for a single-determinantal wave function are given in the Appendix by Eq. (A86).

4. Dynamics of electrons and nuclei

Some time-dependent methods include explicit electronic dynamics as opposed to an averaged electronic description. Examples include (i) dynamics with density-functional theory for electrons and nuclei in condensed phases as proposed by Car and Parrinello (1985); (ii) the time-dependent Hartree-Fock (TDHF) method and variational extensions by Gazdy and Micha (1986); (iii) TDHF for electrons with classical nuclear dynamics on an average potential, developed by Micha and co-workers (Runge *et al.*, 1990; Micha and Runge, 1992; Runge, 1993) for *ab initio* Hamiltonians, by Field (1992) for semiempirical methods, and by Mikkelsen and Ratner (1989) for electron transfer in solvents; (iv) dynamics on an average surface obtained from several adiabatic electronic surfaces (Meyer and Miller, 1979; Olson and Micha, 1984); and (v) close-coupling methods for atomic collisions with one (Fritsch and Lin, 1991) or two electrons treated explicitly (Kimura and Lane, 1990) in the field of atomic collisions.

a. Wave-packet propagation on coupled potential surfaces

Some methods go beyond the restriction of nuclear dynamics on a PES by including one or more excited electronic surfaces. The same methods for exact propagation of wave packets on a single surface have been implemented for two coupled surfaces. The Heidelberg group has made significant contributions in this field (Manthe and Köppel, 1990b; Manthe *et al.*, 1991; Köppel and Manthe, 1992). A fourth-order-difference scheme has been implemented (Manthe and Köppel, 1990a) and has been found to be more efficient than a second-order difference by a factor of 3, but less efficient than the short-time iterative Lanczos formula (Köppel and Manthe, 1992). Multiconfigurational time-dependent Hartree methods with numerical wave-packet propagation on coupled surfaces have also been implemented by Meyer, Cederbaum, and co-workers (Kučar *et al.*, 1987; Meyer *et al.*, 1990; Manthe *et al.*, 1992a, 1992b). These formulations are derived from the TDVP.

A different approach to numerical wave-packet propagation on several surfaces is the method of the wave-packet perturbation theory of Coalson and co-workers, explained in detail in the review of Coalson (1989). This method is well suited for optical spectroscopy in areas where the single-surface approaches break down. In the full formulation, it treats the wave packets on the different surfaces as independent entities. Perturbation theory is used to treat the transfer of probability in space and time between surfaces. This method is not variational.

b. Trajectories on coupled potential surfaces

The method proposed by Meyer and Miller (1979) provides a general framework in which to employ multiple electronic surfaces. It considers only one set of nuclear coordinates moving on the average potential and action-angle variables for electronic degrees of freedom. Olson and Micha (1984), using this approach, employ the real and imaginary parts of the electronic amplitudes as variables.

c. Car-Parrinello method

The method of "parallel dynamics" proposed by Car and Parrinello (1985) was first developed to make simulated annealing more efficient. Later it became quite popular for dynamics simulations. This method was reviewed recently by Remler and Madden (1990) and by Payne *et al.* (1992).

Car and Parrinello add fictitious kinetic-energy terms to obtain dynamical equations for the variables describing the electronic state. This method has caused considerable debate, and there appears to be no clear understanding of why it often works. It is defined by considering the basic parameters describing the electronic state of the system to be the orbitals ψ_i or their coefficients in some appropriate basis. Car and Parrinello apply the method using the density-functional description of extended systems, but, following Remler and Madden in their exposition of the method, we explain the approach in general terms. A Lagrangian for the system of the electronic state and the nuclei is defined as

$$L = T - V + \sum_{ij} \Lambda_{ij}(\langle \psi_i | \psi_j \rangle - \delta_{ij}) \tag{1.4}$$

with Lagrange multipliers to ensure orthonormality of the orbitals throughout the dynamics. The kinetic energy

$$T = \frac{1}{2}\mu \sum_i \langle \dot{\psi}_i | \dot{\psi}_i \rangle + \frac{1}{2} \sum_k M_k \dot{\mathbf{R}}_k^2 \tag{1.5}$$

has the usual terms for the nuclei, but it also has terms for the electronic parameters. This energy is called fictitious by Car and Parrinello and is a purely technical device to derive dynamical equations for the electronic parameters from the above Lagrangian. A system of coupled equations for the nuclei is obtained, which are the familiar molecular-dynamics equations. The approach also gives a set of equations for the electronic parameters which permit the propagation of the electronic state "in parallel" with the nuclear motion. It turns out that this is more efficient than trying to find the new optimal electronic parameters at each geometry; this approach also yields electronic states that are very close to the optimal states at all geometries along the trajectory. In Sec. I.B.4.g, the requirements on parametrization for time-dependent methods are explained in detail. Because Car and Parrinello define their parameters for the electronic state to be real, the only way to obtain equations is by adding the "fictitious" energy which introduces the dependence on $\dot{\psi}$. The proper choice is to use complex parameters. Then the imaginary part is the conjugate variable, the quantum-mechanical electronic energy contains the proper dependence on coordinates and momenta, and the Lagrangian from the time-dependent variational principle gives correct equations without adding terms. The advantage of introducing the fictitious kinetic-energy terms is that one can give the electronic variables a mass comparable to that of the nuclei, or even larger. The resulting dynamics will then have the same time scale as the nuclear motion, which makes the procedure very efficient. As a result, however, the dynamics of the electronic variables bears no relationship to any approximation of the underlying quantum-mechanical dynamics of the electrons.

Hartke and Carter (1992) develop an alternative way to simulate dynamics on a PES along the same general lines and apply it to atomic clusters.

d. Time-dependent Hartree-Fock

There is a large class of methods that are variants of TDHF for the dynamics of electrons and that employ a semiclassical or classical description for the atomic nuclei. Examples are the work of Kulander and collaborators (Kulander *et al.*, 1982; Tiszauer and Kulander, 1984, 1991); of Micha, Feng, and Runge (Runge *et al.*, 1990; Micha and Runge, 1992; Runge, 1993); of Field (1992); and of Mikkelsen and Ratner (1989). All these methods consider an explicit dynamical description of the electronic state. Sometimes the full *ab initio* Hamiltonian is considered (Runge and Micha); sometimes a model Hamiltonian is set up to drive the dynamics (Field, Mikkelsen, and Ratner). The coupling between the electrons and the nuclei in these models is through the (average) potential-energy surface. The nuclei feel the surface and the electrons feel the nuclei only through their instantaneous positions in the Fock operator. As a result, electron momenta are not treated correctly, a deficiency which shows up mainly in higher, nonchemical energy regimes. To remedy this problem, electron translation factors (ETF's) are sometimes introduced (Bates and McCarroll, 1958; Delos, 1981; Fritsch and Lin, 1991; Riera, 1992).

Field has applied TDHF at the semiempirical Austin Model 1 (AM1) level for simulation of the dynamics of LiH, H_2O, and CH_2O molecules (Field, 1992). A brief definition of the semiempirical Hamiltonian used by Field is presented in Sec. 3 of the Appendix. One of the main conclusions of these simulations is that the TDHF-AM1 method gives trajectories that display results for various static and dynamical properties (when a self-consistent-field wave function is chosen as a starting point) that are equivalent to those calculated via trajectories obtained with a method ensuring that the electronic variables satisfy the time-independent variational principle at each time step. Field claims, based on this result, that the TDHF approach has few advantages for the dynamics of closed-shell systems with wave functions lying on or very close to the Born-Oppenheimer surface. This claim is addressed again in the applications section (Sec. IV) after it is shown in Sec. III.A.3 that Field's equations omit the nonadiabatic coupling terms. He has also incorporated the radiation field and radiation-matter interaction at the long-wavelength dipole approximation. As a result, it is possible to study the detailed dynamics of the electronic population in several states when a donor-acceptor molecule is excited by radiation of various wavelengths.

Kulander and co-workers (Kulander *et al.*, 1982; Tiszauer and Kulander, 1984, 1991) describe the electronic orbitals numerically on a grid fixed in space and propagate them together with the classical nuclear positions as a coupled system of difference equations. Their study is restricted to collinear reactions in triatomic systems like $H^+ + H_2$, for which the equation for the (doubly occupied) orbital Φ becomes

$$\begin{aligned} i\frac{\partial}{\partial t}\Phi(\mathbf{r},t) &= h\Phi(\mathbf{r},t) , \\ h &= -\frac{1}{2m}\nabla^2 + V_e(\mathbf{r},t) + V_{ne}(\mathbf{r},t) , \\ V_e(\mathbf{r},t) &= \frac{1}{2}\int \frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}dr' , \\ V_{ne}(\mathbf{r},t) &= \sum_{j=1}^{3} -\frac{1}{|\mathbf{r}-Z_j(t)\mathbf{e}_z|} . \end{aligned} \tag{1.6}$$

The equations used by Runge and Micha (Micha and Runge, 1992; Runge, 1993) introduce an elegant solution to the problem of largely differing time scales in the coupled system of equations. Runge and Micha start from the TDHF equation for the density matrix Γ,

$$i\dot{\Gamma} = F\Gamma - \Gamma F , \tag{1.7}$$

where F is the Fock matrix. The Fock matrix depends linearly on the density matrix and is described in more detail in Eq. (3.23). The nuclei are treated classically and alternatively follow prescribed trajectories, straight lines or Coulomb trajectories, or they follow trajectories computed from

$$M_k\ddot{\mathbf{R}}_k = \nabla_{\mathbf{R}_k}E(R,\Gamma) , \tag{1.8}$$

where the average potential $E(R,\Gamma)$ is the expectation value of the molecular Hamiltonian, including the nuclear repulsion terms and the electronic energy of the state described by the density matrix Γ. To avoid having to integrate the fast electronic motion in Eq. (1.7), Micha and Runge linearize the equation during time steps Δt, long compared to the electronic time scale, but short for the nuclei, with the assumption that the effect of the nuclei is a small perturbation on the evolution of the density matrix. They write $\Gamma(t) = \Gamma^0(t) + \Gamma^1(t)$, where the reference density Γ^0 is propagated assuming that the Fock matrix remains the same as at time t_0

$$i\dot{\Gamma}^0 = F(t_0)\Gamma^0 - \Gamma^0 F(t_0) \tag{1.9}$$

with $F(t_0) = F(R(t_0),\Gamma^0(t_0))$. The correction Γ^1 then gives the effect of the motion of the nuclei, linear in the change of the Fock matrix, on the density

$$i\dot{\Gamma}^1 = F(t_0)\Gamma^1 - \Gamma^1 F(t_0) + \Delta F\Gamma^0 - \Gamma^0\Delta F , \tag{1.10}$$

where $\Delta F = F(R(t),\Gamma^0(t)) - F(t_0)$. These equations are integrated from t_0 to $t_0 + \Delta t$ by diagonalizing $F(t_0)$ and writing Γ^0 and Γ^1 as a superposition of the eigenmodes. An efficient algorithm is used to increase or decrease Δt during the evolution as needed. Runge and Micha write their equations in the traveling atomic-orbital basis, which is important for the quality of their results (Micha and Runge, 1992; Runge, 1993). A more recent treatment (Micha, 1994) using Liouville operators generalizes these equations to all orders in ΔF.

e. Time-dependent density functional

Recently Theilhaber (1992) implemented the rigorous time evolution used in the TDHF in the field of density-functional theory for extended systems as an alternative to the Car-Parrinello method. He describes the electronic system by using Kohn-Sham orbitals and obtains the dynamical equations

$$\begin{aligned} i\frac{\partial}{\partial t}\psi_j(\mathbf{r},t) &= -\frac{1}{2m}\nabla^2\psi_j(\mathbf{r},t) + v_{\text{eff}}(\mathbf{r},t,[n])\psi_j(\mathbf{r},t) , \\ M\frac{d^2}{dt}\mathbf{R}_k(t) &= \mathbf{F}_k(t) , \end{aligned} \tag{1.11}$$

where $\mathbf{F}_k(t)$ is the total force on the kth ion and where, with double occupancy, the density is given by

$$n(\mathbf{r},t) = 2\sum_{j=1}^{N_e/2}|\psi(\mathbf{r},t)|^2 . \tag{1.12}$$

These equations will be studied in detail in Sec. III for the single-determinantal wave function [see Eqs. (3.22)–(3.25)] and are derived from the TDVP in Sec. 1 of the Appendix. More details can be found in Theilhaber's paper (Theilhaber, 1992). He points out that the time-dependent density-functional (TDDF) approach has a physical kinetic energy as opposed to the fictitious kinetic energy of Car and Parrinello (1985). Furthermore, because of the rigorous relation to the Schrödinger equation for the full system, the TDDF equations conserve total momentum and total energy.

To avoid having to integrate the fast electronic motion for long times, Theilhaber uses a procedure well known in the field of plasma physics (Birdsall and Langdon, 1991); i.e., the computer simulations are run with the ion masses equal to $10m_e$, which is small enough to allow for picosecond simulations, but still large enough to ensure approximate adiabaticity of electron motion in response to ion displacements. The results are then rescaled to mass ratios of interest.

f. Close coupling and perturbed stationary state

Reviews of the semiclassical and quantum versions of the close-coupling approach are given by Delos (1981), Kimura and Lane (1990), and Fritsch and Lin (1991). It is a method to describe charge-transfer processes in slow (Delos, 1981) and, recently, also fast (Riera, 1992) atomic collisions. One considers a target system originally at rest at the origin and a projectile atom approaching the target with given impact parameters and velocity. The method concentrates on describing one active electron, the others being frozen in core orbitals or treated by pseudopotentials. Some systems with two active electrons have been studied (Fritsch and Lin, 1991). The semiclassical form of the method is briefly discussed below. Delos (1981) gives a detailed discussion of the fully quantum-mechanical form of the close-coupling method.

The method has three ingredients: (i) a choice of nuclear trajectory, usually a prescribed trajectory, often a straight line or Coulomb trajectory; (ii) a choice of basis set for the electronic wave function; and (iii) the solution of coupled differential equations in time for the coefficients of the electronic wave function. The choice of basis set in the close-coupling method has a rich history reviewed in detail by Fritsch and Lin (1991). The present consensus is to use molecular orbitals ψ_i depending on all nuclear coordinates R with electron translation factors of the form (Kimura and Lane, 1990)

$$F_i(R,\mathbf{r})=\exp[i(m\mathbf{v}\cdot\mathbf{r}f_i(R,\mathbf{r})-mv^2t/2)/\hbar] \tag{1.13}$$

with a switching function f, which has the asymptotic values ± 1 for the limit where the two atoms are far apart. The space-independent kinetic-energy term can be left off and incorporated in the wave-function expansion coefficients. The question of ETF's is addressed in detail in Sec. II.A.

The total molecular wave function is then written as

$$\Psi(R,\mathbf{r})=\sum_i \chi_i(R)\psi_i(R,\mathbf{r})F_i(R,\mathbf{r}) \ . \tag{1.14}$$

In the semiclassical approximation, this becomes

$$\Psi(R,\mathbf{r})=\sum_i a_i(t)\psi_i[R(t),\mathbf{r}]F_i[R(t),\mathbf{r}]\exp(f) \ , \tag{1.15}$$

where

$$f=-i\int^t E_i[R(t')]dt'-\frac{1}{2}\int^t v^2 dt' \ . \tag{1.16}$$

Substituting Eq. (1.15) in the time-dependent Schrödinger equation, projecting on the electronic basis, and expanding to first order in $\mathbf{v}$ give the coupled equations

$$iS\frac{da}{dt}=[h+\vec{v}\cdot(\mathbf{P}+\mathbf{A})]a \tag{1.17}$$

with

$$\begin{aligned}
&S_{ji}=\langle\psi_jF_j|\psi_iF_i\rangle \ ,\\
&\mathbf{P}_{ji}=\langle\psi_j|-i\sum_k \nabla_{\mathbf{R}_k}|\psi_i\rangle \ ,\\
&\mathbf{A}_{ji}=\langle\psi_jF_j|[h_{\mathrm{el}},\mathbf{r}f_i(R,\mathbf{r})]|\psi_iF_i\rangle \ ,\\
&h_{ji}=\langle\psi_j|h_{\mathrm{el}}|\psi_i\rangle \ .
\end{aligned} \tag{1.18}$$

The total Hamiltonian is defined as $H(R,\mathbf{r})=T+h_{\mathrm{el}}$, with T the appropriate nuclear kinetic-energy operator. The nonadiabatic coupling terms $\mathbf{P}$ are derived for a single-determinant wave function in the Appendix, Sec. 2.c, Eq. (A67). A related term, Eq. (A68), that acts on the nuclear motion, also is obtained there, but not considered in close-coupling treatments where the nuclei are assumed to move on prescribed trajectories.

Note that the ETF's are used to derive the terms $\mathbf{A}$, but are neglected in the evaluation of $\mathbf{P}$ and $\mathbf{h}$. This is because the term $\mathbf{A}$ is essential for obtaining the correct asymptotic behavior of the equations, whereas the low velocity makes the ETF almost equal to unity in the volume over which the matrix elements $\mathbf{P}$ and $\mathbf{h}$ are evaluated. It is then a good approximation to omit the ETF in that integration. See Riera (1992) and Fritsch and Lin (1991) for a detailed discussion.

The perturbed-stationary-state (PSS) method (Mott and Massey, 1965) was the first formulation (without ETF's) of the close-coupled equations for electronic dynamics in atomic collisions. Modern applications of the PSS method do include proper treatment of the velocity (Riera, 1992). The original PSS equations have only the nonadiabatic coupling term $\mathbf{P}$ of Eq. (1.18) and rely on the completeness of the basis to accurately represent the other terms. The correct inclusion of ETF's (Delos, 1981) essentially brings out all terms linear in the nuclear velocities and is therefore less sensitive to the basis used.

g. Electron-nuclear dynamics

The theory of electron-nuclear dynamics (END; Deumens and Öhrn, 1988; Deumens, Diz, Taylor, and Öhrn, 1992; Öhrn *et al.*, 1992; Longo *et al.*, 1993) has a more elaborate and detailed mathematical foundation than most time-dependent treatments of the dynamics of electrons and nuclei in molecules. The payoff for the additional work is a deeper understanding of the structure of the dynamical equations. For example, the END analysis straightforwardly produces terms that have been found to be essential in some atomic collision work for describing higher-energy processes. These terms have an extensive history and are related to the correct treatment of the electron translation factors (Bates and McCarroll, 1958; Delos, 1981). In END these terms are obtained by a straightforward coordinate transformation in the phase space of the molecular-state parameters. This conceptual simplification has practical and didactic advantages over the conventional ETF derivation.

The mathematical tools for defining and analyzing the phase space include the theory of Lie groups, coherent states, and dynamical systems (Kramer and Saraceno, 1981; Klauder and Skagerstam, 1985; Perelomov, 1986). The term "coherent" comes from laser theory, where Glauber used special wave functions to describe the coherence of light. The mathematical generalizations of the wave functions used by him are still called coherent states, but they rarely have any physical property of coherence. Rather, one can think of the term as referring to the mathematical property of the resolution of the identity. Mathematically, coherent states are an overcomplete set with a resolution of the identity. The fact that all states in the overcomplete set add up to unity makes the set "coherent." The understanding of the theory of coherent states and Lie groups is in no way essential to the understanding or use of the theory, or to the derivation of the physical properties of the equations. The theory of coherent states is inspiring and important in order to find the optimal parametrization of the wave function. It is also useful in proving the internal consistency of the equations. Coherent states and Lie groups are not introduced in this presentation of time-dependent treatments, but their relevance is clarified in Sec. II.B.2 for the interested reader.

The END theory can be considered as an extension of the TDHF methods in the sense that electrons and nuclei are allowed to interact without any restriction, as opposed to methods with a potential surface construction and the associated averaging over electronic motion. This implies, among other things, that neither the Born-Oppenheimer nor the adiabatic approximation is enforced in END and that (even with classical nuclei) the trajectories are truly dynamical and result from the action of the instantaneous forces.

END differs from other time-dependent methods proposed and developed in recent years in that it recognizes that the electron-nuclear dynamics takes place in a generalized phase space. The detailed analysis of this phase space and the explicit construction of its metric are important ingredients in the END approach. Other methods assume, implicitly, that the phase space is canonical, i.e., flat. In some cases, that may be correct; in others, though, this requires further investigation. For instance, when ETF's are important, the correct forces that have caused significant debate and that can be derived from ETF's by sometimes laborious schemes (Delos, 1981) are actually contained in the phase-space metric. The formulation of the dynamics in the proper phase space greatly clarifies the dynamical origin of these terms and simplifies their derivation.

The principles of END are few and simple.

(1) Parametrize a wave function for the molecule as a whole, i.e., for electrons and nuclei. Make sure that (a) the parameters are nonredundant; (b) the parameters are divided into coordinates and their conjugate momenta; and (c) the parameters generate a complete set of wave functions.

(2) Make all parameters time dependent and derive dynamical equations for them using the chosen parametrized wave functions as the family of allowed variations in the TDVP. Although several types of wave functions have been considered (Deumens *et al.*, 1987a, 1991; Deumens and Öhrn, 1989b; Weiner *et al.*, 1991), this review concentrates for several reasons on the simplest possible choice, i.e., a single determinant—spin unrestricted and with complex coefficients—for the electrons and a classical treatment of the nuclei.

Among the reasons for this choice are the following: (i) It is general enough to exhibit most intricacies of time-dependent treatments explicitly; (ii) the choice is sufficiently rich to allow a meaningful comparison with experiments for a large variety of physical and chemical processes; (iii) the general framework generated by the choice includes many of the most widely used methods as special cases; and (iv) necessary generalizations can be formulated as conceptually simple extensions, but would be cumbersome to discuss for the purposes of a review.

The parameters should be such that each quantum-mechanical state, i.e., each wave function up to a normalization constant and global phase factor, is mapped one-to-one on a set of parameter values. For TDHF, one often uses molecular-orbital coefficients. Because of the well-known invariance of a determinantal state under arbitrary transformations of the occupied (and unoccupied) orbitals among themselves, there are many parameter values that represent the same state. Because the Schrödinger equation determines the evolution of quantum states, it is invariant under any transformation that leaves states invariant. As a result, the equations for the parameters derived from the TDVP will be invariant as well. It follows that such equations will not determine the evolution of redundant parameters. This leads to numerical instabilities. These can be eliminated by appropriate constraints. However, it is obvious that the system with constraints will be less efficient than a straightforward propagation of a set of nonredundant parameters. For a single determinant, the theory of coherent states associated with the unitary group of the single-particle space immediately yields the correct parameters (Kramer and Saraceno, 1981). These parameters are known in nuclear physics as the Thouless representation (Thouless, 1960) of a determinantal state and are used in the classification of spin- and charge-density waves in solid-state theory (Fukutome, 1981). Their construction is presented in Sec. II.B, and in Sec. III.C.2 it is proven that they can be interpreted as random-phase-approximation (RPA) amplitudes (Linderberg and Öhrn, 1973).

The second requirement on the parameters is that they be suitable to describe a dynamical system. The Schrödinger equation in Hilbert space is an infinite-dimensional, linear dynamical system, and the complex nature of Hilbert space is essential. For the time-dependent treatment to retain that essential feature, it is necessary and sufficient that the parameters form a phase space, which means they can be divided into a set of coordinates and a set of conjugate momenta. Such a division is called a symplectic structure and is the foundation of the theory of dynamical systems (Goldstein, 1980). Imposition of such a structure ensures that the time-dependent treatment, however approximate, will be dynamically reasonable. The elements of the one-particle density matrix provide a choice of parameters (coordinates) for a single-determinantal wave function (Runge, 1993). However, no conjugate momenta exist and therefore some inconsistencies can be expected for such a choice. Because Runge and Micha use a linearized form of the equations to propagate the electronic coordinates, they implicitly use conjugate momenta that are, as for any oscillator, $\pi/2$ out of phase; and no problems arise. Were one to attempt a solution of the nonlinear equations, one must define conjugate momenta for the electronic degrees of freedom. When the theory of coherent states and Lie groups is used, the existence of the symplectic structure is guaranteed—another advantage of using these mathematical tools.

The third requirement is that the parameters be such that the wave functions for all possible parameter values, in principle, form a complete set. It is formally overcomplete because of the continuity of the parameters.

In our case this means that the single-determinantal wave function for the electrons is

$$\det(\chi_h(\mathbf{r}_n)) \tag{1.19}$$

with

$$\chi_h(\mathbf{r})=\psi_h(\mathbf{r})+\sum_p \psi_p(\mathbf{r})z_{ph} , \tag{1.20}$$

where the $\psi_k(\mathbf{r})$, $k=p,h$, are appropriate orthonormal two-component spin-orbitals expressed in some (in principle, complete) basis of spin-orbitals. This parametrization ensures that during the time evolution of the z parameters the system will be able to access all possible determinantal wave functions in the given orbital basis. Theoretically the most convenient orbital basis would be a fixed orthonormal set. This leads to simple dynamical equations. One choice would be harmonic-oscillator eigenfunctions centered at the origin. They are complete, orthonormal, and easy to work with. On the other hand, from the point of view of computations, a description is desired with physical quantities represented accurately by a small number of terms. Since representations of orbitals on one center in a basis located at another center converge poorly, electronic structure theory works with atomic orbitals on all centers. The same idea works for dynamical problems with appropriate adjustments of the dynamical equations. Electron translation factors are a similar convergence accelerating device. When used with the correct dynamical equations, they are nothing more. Details are discussed in Sec. II.A.

With a given choice of the form of the wave function and with a choice of parameters (including orbital basis), all approximations are specified. The derivation and solution of the equations involve no further approximations.

II. PREPARATIONS

All treatments of molecular systems use quantum mechanics to describe the electrons. Some methods only look at the electrons through the electronic eigenstates associated with the PES's; others treat the electronic degrees of freedom dynamically. Although the methods that currently use fitted surfaces have integrated out all detailed electronic information, the more exact ones, like the pseudospectral Fourier approximation, are expected to include eventually an explicit treatment of the electrons as a way to overcome the limitations of the fitting procedure. Furthermore, all methods that do include a full treatment of the electrons need to be supplied with an initial state for the evolution. This is often a molecular state including an electronic state on the PES. A thorough understanding of how the electrons are described is essential for all time-dependent methods. This is the subject of Secs. II.A and II.B.

Next, the description of the nuclei is discussed in Sec. II.C, and finally, in Sec. II.D, a detailed discussion of the time-dependent variational principle (TDVP) is given.

A. Electronic spin-orbitals

1. Choice of basis and convergence

An approximate many-electron wave function can be represented in a variety of ways. Both for the ease of interpretation in terms of chemical and physical concepts and for computational efficiency, it is convenient to build many-electron wave functions from single-particle functions or spin-orbitals. These orbitals are, in general, chosen to be expressed in terms of a basis set of functions of some analytic form that can be efficiently manipulated. In principle, one could represent the many-electron functions on a grid and obtain an "exact" numerical representation. However, the number of grid points increases so rapidly with the number of electrons, that this technique has never been applied successfully to more than one or two electrons.

The choice of basis set in terms of which to represent the spin-orbitals has been given much consideration in quantum chemistry. Excluding electron scattering or ionization processes, it is clear that electronic density remains near the atomic nuclei throughout a process. If one considers the number of basis functions of some type, say, harmonic-oscillator-type functions centered at the origin, needed to represent an orbital located on a nucleus some distance removed, it becomes clear that it is more efficient to analytically move the basis functions over to the atomic nucleus. When one centers basis functions on a number of different nuclei in that way, the resulting total basis is no longer orthonormal and can introduce annoying approximate linear dependencies; however, it is known in practice to work quite well for general molecular systems. Thus using basis functions centered on the atomic nuclei rather than on fixed points in space is an obvious choice that leads to better convergence properties.

A similar observation holds with regard to convergence of a basis for the velocity or momentum properties of the electrons. Given the properly derived equations of motion, convergence is accelerated by analytically moving the basis function to the atomic nuclei in phase space, rather than just in configuration space. This simplifies and explains the role of electron translation factors, a subject that has received considerable attention in the time-dependent formulations (Delos, 1981).

2. Atomic spin-orbitals

The electronic wave function is ultimately defined in terms of a set of K localized atomic spin-orbitals. These spin-orbitals are given as linear superpositions of exponential or Gaussian functions, to describe the spatial part, multiplied by an α or β spin function for the spin part or a completely general two-component spinor function. *In this paper a spin function is assumed always to be included or a general two-component function is considered and the terms spin-orbital and orbital are used interchangeably.* An orbital is called a Slater-type orbital if it has the form

$$x^k y^l z^m r^j \exp(-\alpha r) \tag{2.1}$$

and a Gaussian-type orbital if it is expressed as

$$x^k y^l z^m \exp(-\alpha r^2) \ , \tag{2.2}$$

where $\mathbf{r}=(x,y,z)$ is the electron coordinate. The orbitals are, in general, centered on one of the atomic nuclei and are therefore referred to as *atomic orbitals.* But they can be centered, in principle, anywhere in space, for example, to describe bonds. These orbitals are nonorthogonal.

The choice of basis, Slater-type orbital or Gaussian-type orbital, depends on which of their properties are most valuable for a particular type of computation. Both sets can, in principle, be extended to a complete basis for a single-particle Hilbert space and are in that sense equivalent. However, the following properties are relevant to electronic structure and dynamics. The Slater-type orbitals have (1) the correct asymptotic behavior of r at large distances for appropriate choices of α, namely, exponential decay; (2) the correct behavior at the atomic nucleus if appropriate exponents α and linear combinations have been chosen to satisfy the cusp condition; (3) analytic expressions for one- and two-center matrix elements, including the Coulomb potential, but not for elements involving more centers; and (4) no analytic expressions for matrix elements that include an exponential plane-wave factor.

The Gaussian-type orbitals, on the other hand, have (1) the wrong asymptotic behavior for molecules at large distances; (2) the wrong behavior at the atomic nucleus because their derivative is always zero; and (3) analytic expressions for all matrix elements of the electron-electron Coulomb repulsion, even with inclusion of an exponential plane-wave factor.

Slater-type orbitals have superior qualities for appropriate choices of exponent factors α, but are computationally demanding for *ab initio* applications (because of the three- and four-center matrix elements). They are used primarily for calculations on atomic and diatomic systems. Slater-type orbitals are also employed in semiempirical theories, which neglect all but one-center matrix elements, such as the intermediate neglect of differential overlap method, or all but one- or two-center matrix elements, such as the neglect of diatomic differential overlap method. The asymptotic behavior of the orbitals is crucial for the computations of electron-transfer-matrix elements which depend strongly on the tail of the electronic wave functions. The necessary matrix elements have been coded in parametrized schemes as ZINDO (Zerner, 1991), AMPAC (Dewar *et al.*, 1985), and MOPAC (Stewart, 1990).

Ab initio calculations on general molecular systems employ Gaussian-type orbitals for efficient evaluation of all matrix elements with small superpositions (contractions) of a few *primitive* Gaussian-type orbitals. Matrix elements and associated integrals over Gaussian-type orbitals are evaluated with the algorithms of McMurchie and Davidson (1978) in SIRIUS by Helgaker, Jensen, and Ågren (Helgaker *et al.*, 1986) and in DISCO by Feyereisen (Feyereisen and Kendall, 1993), and with the algorithms of Obara and Saika (1988) in GAUSSIAN by Pople and co-workers (Gill and Pople, 1991) and in other quantum chemistry integral codes.

3. Molecular spin-orbitals

Most manipulations with wave functions for many electrons are conveniently carried out in an orthonormal basis $\{\psi_i\}_{i=1,\ldots,K}$. Let $\{\phi_i\}_{i=1,\ldots,K}$ be a set of atomic spin-orbitals. The orthonormal basis is sometimes referred to as the *molecular-orbital basis* because such orbitals are spread out over the system. In practice, orthonormal molecular orbitals are obtained by either a simple orthonormalization procedure or some construction that relates more closely to the physics of the problem, such as the orbitals that diagonalize the Fock operator. The use of orthonormal orbitals yields a clear and simple derivation of the dynamical equations. However, computational efficiency demands that the dynamical equations be transformed to the atomic-orbital basis for *ab initio* Hamiltonians.

The relation between these two bases is

$$\psi=\phi W \ , \tag{2.3}$$

where ψ and ϕ are row arrays of basis functions. Thus the transformation is defined so that the columns of the matrix W represent the new basis vectors. The transformation matrix W satisfies

$$W^\dagger \Delta W = I \ , \tag{2.4}$$

where the atomic overlap matrix Δ has the elements

$$\Delta_{ij}=\langle \phi_i | \phi_j \rangle = \int \phi_i^*(\mathbf{r})\phi_j(\mathbf{r}) d^3 r \ ; \tag{2.5}$$

i.e., $WW^\dagger=\Delta^{-1}$.

The electron field operators

$$F(\mathbf{r})=\sum_{i=1}^{K}\psi_i(\mathbf{r})b_i=\psi b=\phi WW^{\dagger}a \tag{2.6}$$

are introduced, and the basis field operators transform as

$$b=W^{\dagger}a\ , \tag{2.7}$$

where the spin-orbitals and basis creation operators are arranged in a row array. This means that the creators transform as the spin-orbital basis. It then follows that (Linderberg and Öhrn, 1973)

$$\begin{aligned}&[b,b^{\dagger}]_{+}=1\ ,\\&[a,a^{\dagger}]_{+}=\Delta\ .\end{aligned} \tag{2.8}$$

Thus the anticommutation relations

$$\begin{aligned}[F(\mathbf{r}),F^{\dagger}(\mathbf{r}')]_{+}&=\psi(\mathbf{r})[b,b^{\dagger}]_{+}\psi^{\dagger}(\mathbf{r}')\\&=\phi(\mathbf{r})\Delta^{-1}[a,a^{\dagger}]_{+}\Delta^{-1}\phi^{\dagger}(\mathbf{r}')\\&=\delta(\mathbf{r}-\mathbf{r}')\end{aligned} \tag{2.9}$$

hold as they should for fermion field operators. The last step is true only in a complete basis.

A single-determinantal state

$$|\Psi_0\rangle=|(b_1^{\dagger}\cdots b_N^{\dagger})\rangle=\prod_{h=1}^{N}b_h^{\dagger}|\text{vac}\rangle\ , \tag{2.10}$$

where the product $\prod_{h=1}^{N}b_h^{\dagger}$ refers to an ordered set of creation operators, has the wave function (Linderberg and Öhrn, 1973)

$$\begin{aligned}\Psi_0(\mathbf{r}_1,\ldots,\mathbf{r}_N)&=\langle\text{vac}|\prod_{n=1}^{N}F(\mathbf{r}_n)|\Psi_0\rangle\\&=\langle\text{vac}|\prod_{n=1}^{N}F(\mathbf{r}_n)\prod_{h=1}^{N}b_h^{\dagger}|\text{vac}\rangle\\&=\det\{\psi_h(\mathbf{r}_n)\}\end{aligned} \tag{2.11}$$

for the case of the orthonormal spin-orbitals, and

$$\begin{aligned}\Psi_0(\mathbf{r}_1,\ldots,\mathbf{r}_N)&=\langle\text{vac}|\prod_{i=1}^{N}F(\mathbf{r}_n)\prod_{h=1}^{N}a_h^{\dagger}|\text{vac}\rangle\\&=\det\{\phi_h(\mathbf{r}_n)\}\end{aligned} \tag{2.12}$$

for the case of the nonorthogonal basis. The chosen form of the field operators, Eq. (2.6), in the nonorthogonal basis ensures the parallel behavior to that of the orthogonal basis in the manipulation of determinantal wave functions.

The expectation value of the electronic position is given by

$$\begin{aligned}&\int\langle\Psi_0|F(\mathbf{r})^{\dagger}\mathbf{r}F(\mathbf{r})|\Psi_0\rangle d^3r/\langle\Psi_0|\Psi_0\rangle\\&\quad=\sum_{i,j=1}^{K}\int\psi_i^{*}(\mathbf{r})\mathbf{r}\psi_j(\mathbf{r})d^3r\langle\Psi_0|b_i^{\dagger}b_j|\Psi_0\rangle/\langle\Psi_0|\Psi_0\rangle\\&\quad=\sum_{i,j=1}^{K}r_{ij}\Gamma_{ji}=\text{Tr}(r\Gamma)\ ,\end{aligned} \tag{2.13}$$

and similarly for the electronic momentum with the matrix elements

$$p_{ij}=\frac{\hbar}{i}\int\psi_i(\mathbf{r})^{*}\nabla_{\mathbf{r}}\psi_j(\mathbf{r})d^3r\ . \tag{2.14}$$

4. Electron translation factors

In his review, Delos (1981) has explained in detail the structure and role of electron translation factors (ETF's). When electronic wave functions, determined as eigenfunctions of the static electronic Hamiltonian, are used as basis functions for a time-dependent treatment of the molecule, it is necessary to take into account the proper transformation of the electronic basis functions from being centered on a fixed point near a nucleus to moving along with that nucleus. Since the problem, and the solution, is the same for a classical description of the nuclei as it is for a quantum-mechanical treatment, only the classical case is discussed here and the reader is referred to Delos's review for more details. An ETF is given by

$$\exp[i(m\mathbf{v}\cdot\mathbf{r}-mv^2t/2)/\hbar]\ . \tag{2.15}$$

The term with the kinetic energy is just a time-dependent phase factor and is important only when the ETF's are used to derive the correct dynamical equations. This aspect is not discussed further in this section. Multiplying an atomic orbital with the ETF of the form

$$\beta=\exp[im\mathbf{v}\cdot\mathbf{r}/h] \tag{2.16}$$

results in what is called a *traveling atomic orbital.*

The use of ETF's for molecular orbitals has been the subject of debate for some time (Kimura and Lane, 1990; Fritsch and Lin, 1991; Riera, 1992) because the method of implementation is not as obvious as it is for atomic orbitals. There is some consensus that the form of Eq. (1.13) is adequate (Delos, 1981; Fritsch and Lin, 1991). The physical role of the ETF is explained clearly by Riera (1992) to be that it adds the necessary flux to the static orbitals (atomic or molecular), which are usually real, to make them suitable for the description of molecules in motion.

Traveling Slater-type orbitals and Gaussian-type orbitals can be defined. However, only traveling Gaussian-type orbitals are of any practical use, since it is possible to evaluate the necessary matrix elements over them analytically as shown by Obara and Saika (1988). It is unfortunate that this aspect of their paper seems not to have been implemented in any general-purpose code. Most computations using ETF's reported to date employ them to get the correct equations, but neglect them in the multicenter Coulomb integrals (Fritsch and Lin, 1991; Riera, 1992). The main argument is that the de Broglie wavelength is large compared to the size of the atomic orbitals; so the ETF can be assumed constant over the volume of integration where the integrand is significant. The same argument also justifies using an expansion,

$$\exp(i\mathbf{k}\cdot\mathbf{r})\varphi_{k,l,m}(a,\mathbf{r})=\varphi_{k,l,m}(a,\mathbf{r})+i\mathbf{k}\cdot\mathbf{r}\varphi_{k,l,m}(a,\mathbf{r})+\cdots$$

$$=\varphi_{k,l,m}(a,\mathbf{r})+ik_x\varphi_{k+1,l,m}(a,\mathbf{r})+ik_y\varphi_{k,l+1,m}(a,\mathbf{r})+ik_z\varphi_{k,l,m+1}(a,\mathbf{r})+\cdots\ , \tag{2.17}$$

of the ETF. For small to moderate velocities, truncations of this expansion are adequate. This is basically the assumption in the perturbed-stationary-states approach (Riera, 1992).

The fact that Slater-type-orbital matrix elements with ETF's cannot be evaluated analytically makes this expansion of the ETF the only feasible option in semiempirical theories or *ab initio* methods using Slater-type orbitals.

B. Electronic wave function

The electronic wave function used to construct a PES or to describe the electrons dynamically can be chosen in many forms. The comparison of various choices encompasses the entire field of electronic structure theory. For the purpose of time-dependent treatments of molecular systems, only a few general observations need to be made. As larger molecular systems are considered, it becomes harder to find a usable fitted surface. Because of this, the techniques that consider the nuclear dynamics on a PES probably have to abandon the construction of the surface. One might therefore expect that all time-dependent dynamical approaches would eventually include an explicit treatment of the electrons in some form or other. It is important in such an approach to have a consistent, balanced approximation for the electrons, i.e., one that shows good relative energies such as barrier heights, while it may be less important that the total energies be accurate.

When electronic wave functions are employed, either to produce the PES and its gradients or to provide explicit electronic dynamics, their parametrization becomes important. Because of its simplicity and its success in practical applications, the case of a single spin-unrestricted complex determinantal wave function is considered (Deumens and Öhrn, 1989b). Such a wave function is quite approximate, particularly if one is concerned with total energies and correlation effects; however, for many systems, its qualitative features are right, and therefore it is worthwhile to explore its use in this context both for didactic purposes and for some nontrivial applications. All basic ingredients needed for a proper treatment of more general wave functions—such as the multiconfigurational ones (Deumens *et al.*, 1991), the spin-projected Hartree-Fock (Weiner *et al.*, 1991), and the antisymmetrized geminal power ones (Deumens *et al.*, 1987a)—are present already in the single-determinantal case (Deumens, Diz, Taylor, and Öhrn, 1992).

The concept of coherent states with the theory of Lie groups exposes the properties of a determinant that seem special, and it shows that these properties are quite general and apply to other forms of wave functions as well. It is not essential for an understanding of the physics in this paper to be familiar with the concept of coherent states; hence Sec. II.B.2 may be skipped at first reading.

Proper parametrization means the following: (1) The parameters (or labels) of the electronic wave function must be minimal or nonredundant; (2) in order to describe electron dynamics, the parameters must exhibit the structure of a phase space with pairs of conjugate coordinates and momenta; and (3) the parameter manifold should be continuous and able to generate a complete set of states, i.e., states that provide a resolution of the identity.

1. Dynamic orbitals

In the context of a determinantal state, it is meaningful to divide the set of K spin-orbitals into N *occupied* and K-N *unoccupied* spin-orbitals. When a linear array q refers to the set of all, of only occupied, or of only unoccupied spin-orbitals, it is denoted by q, $q^{\bullet}$, and q°, respectively.

Atomic spin-orbitals may also be partitioned into two sets which may be called occupied and unoccupied. This should be understood as a mere mathematical construct. For the purpose of dynamics, the reference determinant is simply made up of nonorthogonal atomic spin-orbitals which are said to be "occupied." The rest are "unoccupied." The reference determinant does not necessarily have any physical meaning. It only provides a suitable mathematical reference. With this in mind, the atomic spin-orbitals can be partitioned as follows,

$$\phi=(\phi^{\bullet}\ \ \phi^{\circ})\ . \tag{2.18}$$

Similarly, for matrices, four sub blocks are identified: the occupied $N\times N$ and unoccupied $(K\text{-}N)\times(K\text{-}N)$ diagonal blocks, and the upper and lower off-diagonal blocks. The transformation to the molecular basis becomes, in block form,

$$(\psi^{\bullet}\ \ \psi^{\circ})=(\phi^{\bullet}\ \ \phi^{\circ})\begin{bmatrix} W^{\bullet} & W^{>} \\ W^{\vee} & W^{\circ} \end{bmatrix}\ . \tag{2.19}$$

A solid circle is used to denote the occupied part and an empty circle to denote the unoccupied part. The superscript $>$ denotes the upper off-diagonal block, reminding us of the horizontal rectangular shape with the number of occupied orbitals (the number of rows of that block) usually being smaller than the number of unoccupied orbitals (the number of columns). Similarly, the superscript $\vee$ denotes the lower off-diagonal block, which has a vertical rectangular shape, where the opposite is true. With this notation many messy index manipulations are avoided. As a mnemonic device, p,q,r are reserved for indices running over the *particle* or unoccupied range $N+1,\ldots,K$, and h,g,f for the *hole* or occupied range $1,\ldots,N$.

Introducing a general unitary transformation U of the orthonormal spin-orbital basis, one can write

$$(c^{\bullet\dagger}\;\; c^{\circ\dagger})=(b^{\bullet\dagger}\;\; b^{\circ\dagger})\begin{bmatrix} U^{\bullet} & U^{>} \\ U^{\vee} & U^{\circ} \end{bmatrix} \tag{2.20}$$

for the basis field operators and obtain, following Thouless (1960), for a determinantal state (Deumens and Öhrn, 1989b),

$$\begin{aligned}
|\Psi\rangle=|c^{\bullet\dagger}\rangle&=\prod_{h=1}^{N} c_h^{\bullet\dagger}|\mathrm{vac}\rangle\\
&=\prod_{h=1}^{N}\left[\sum_{k=1}^{N} b_k^{\bullet\dagger}U_{kh}^{\bullet}+\sum_{p=N+1}^{K} b_p^{\circ\dagger}U_{ph}^{\vee}\right]|\mathrm{vac}\rangle\\
&=\prod_{h=1}^{N}\left[\sum_{l=1}^{N}\left[b_l^{\bullet\dagger}+\sum_{p=N+1}^{K}\sum_{k=1}^{N} b_p^{\circ\dagger}U_{pk}^{\vee}U_{kl}^{\bullet-1}\right]U_{lh}^{\bullet}\right]|\mathrm{vac}\rangle\\
&=\alpha\prod_{h=1}^{N}\left[b_h^{\bullet\dagger}+\sum_{p=N+1}^{K}\sum_{k=1}^{N} b_p^{\circ\dagger}U_{pk}^{\vee}U_{kh}^{\bullet-1}\right]|\mathrm{vac}\rangle\\
&=\alpha\prod_{h=1}^{N}\left[1+\sum_{p=N+1}^{K}\sum_{k=1}^{N} b_p^{\circ\dagger}U_{pk}^{\vee}U_{kh}^{\bullet-1}b_h^{\bullet}\right]\prod_{l=1}^{N} b_l^{\bullet\dagger}|\mathrm{vac}\rangle\ ,
\end{aligned} \tag{2.21}$$

where the invariance, up to a constant α, of a determinantal wave function under a linear transformation of its occupied spin-orbitals is used. Defining $\sum_{k=1}^{N} U_{pk}^{\vee}U_{kh}^{\bullet-1}=z_{ph}$, and the reference state

$$|\Psi_0\rangle=|b^{\bullet\dagger}\rangle=\prod_{h=1}^{N} b_h^{\bullet\dagger}|\mathrm{vac}\rangle\ , \tag{2.22}$$

one can write the un-normalized state

$$\begin{aligned}
|z\rangle&=\prod_{h=1}^{N}\left[1+\sum_{p=N+1}^{K} b_p^{\circ\dagger}z_{ph}b_h^{\bullet}\right]|\Psi_0\rangle\\
&=\prod_{h=1}^{N}\prod_{p=N+1}^{K}(1+b_p^{\circ\dagger}z_{ph}b_h^{\bullet})|\Psi_0\rangle\\
&=\prod_{h=1}^{N}\prod_{p=N+1}^{K}\exp(z_{ph}b_p^{\circ\dagger}b_h^{\bullet})|\Psi_0\rangle\\
&=\exp\left[\sum_{h=1}^{N}\sum_{p=N+1}^{K} z_{ph}b_p^{\circ\dagger}b_h^{\bullet}\right]|\Psi_0\rangle\ .
\end{aligned} \tag{2.23}$$

In Eq. (2.23) the nilpotency of the operators $b_p^{\circ\dagger}b_h^{\bullet}$ is exploited.

The determinantal wave function of this state is $\det\{\chi_h(\mathbf{r}_n)\}$ in terms of the occupied *dynamical orbitals*

$$\chi_h=\psi_h+\sum_{p=N+1}^{K}\psi_p z_{ph}\ . \tag{2.24}$$

These orbitals are not orthogonal.

The parameters satisfy the stated conditions. By eliminating the transformation among occupied orbitals, one makes sure that the z's are nonredundant. This could pose a problem if the dynamics wants to change orbitals so that the original reference orbitals are no longer participating, which results in some of the z's getting very large. The problem is resolved in the computer code implementation by switching to new reference orbitals.[1] The numerical evolution is more stable and faster if the z's are kept small. For that reason coordinate charts are switched when the norm of the z's reaches about 100 rather than when they reach magnitudes that would involve the machine precision (usually around 10^{13}).

It was shown by Broeckhove and co-workers (Broeckhove *et al.*, 1988) that complex parameters always admit a symplectic structure; hence the choice satisfies requirement number 2.

Since the reference is an arbitrary determinant, it follows that all determinants in the spin-orbital basis can be represented in Thouless form. It is then possible to show, as is done in the next section, that the Thouless parameters can generate a complete set and thus satisfy the third requirement.

In order to find a set of virtual dynamical orbitals that are orthogonal to the occupied space, the following matrix product is considered,

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[1] This can be viewed, in the language of differential geometry, as moving from one coordinate chart to the next. This system of charts is valid because the Thouless parameters, with respect to one reference state, depend analytically on Thouless parameters defined with respect to another reference state, provided the two reference states have nonzero overlap. This is a simple consequence of the SU(K) group composition law expressed in Thouless parameters.

$$\begin{bmatrix} I^\bullet & z^\dagger \\ -z & I^\circ \end{bmatrix}\begin{bmatrix} I^\bullet & -z^\dagger \\ z & I^\circ \end{bmatrix} = \begin{bmatrix} I^\bullet+z^\dagger z & -z^\dagger+z^\dagger \\ -z+z & I^\circ+zz^\dagger \end{bmatrix} = \begin{bmatrix} I^\bullet+z^\dagger z & 0 \\ 0 & I^\circ+zz^\dagger \end{bmatrix} . \tag{2.25}$$

This shows that the partitioned matrix

$$\begin{bmatrix} I^\bullet & -z^\dagger \\ z & I^\circ \end{bmatrix} \tag{2.26}$$

defines the coefficients of dynamic occupied and virtual orbitals spanning mutually orthogonal spaces. It follows that the projectors on these spaces add up to the unit operator. One can then write

$$I-P_{\text{occ}}=P_{\text{virt}} , \tag{2.27}$$

explicitly

$$\begin{aligned} I-\begin{bmatrix} I^\bullet \\ z \end{bmatrix}(I^\bullet+z^\dagger z)^{-1}(I^\bullet \;\; z^\dagger) &= \begin{bmatrix} -z^\dagger \\ I^\circ \end{bmatrix}(I^\circ+zz^\dagger)^{-1}(-z \;\; I^\circ) \\ &= \begin{bmatrix} I^\bullet-(I^\bullet+z^\dagger z)^{-1} & -(I^\bullet+z^\dagger z)^{-1}z^\dagger \\ -z(I^\bullet+z^\dagger z)^{-1} & I^\circ-z(I^\bullet+z^\dagger z)^{-1}z^\dagger \end{bmatrix} \\ &= \begin{bmatrix} z^\dagger(I^\circ+zz^\dagger)^{-1}z & -z^\dagger(I^\circ+zz^\dagger)^{-1} \\ -(I^\circ+zz^\dagger)^{-1}z & (I^\circ+zz^\dagger)^{-1} \end{bmatrix} . \end{aligned} \tag{2.28}$$

The unoccupied dynamical orbitals are consequently written as

$$\chi_p=\psi_p-\sum_{h=1}^{N} z^*_{ph}\psi_h , \tag{2.29}$$

and, although mutually nonorthogonal, they are orthogonal to the occupied space. This orthogonality and the relations implied between the various blocks of the partitioned matrices in Eq. (2.28) are often used in the following to simplify various expressions.

2. Coherent states and Lie groups

In this section the determinantal wave function is treated as a coherent state (Deumens and Öhrn, 1989b), and the meaning of the wave-function parameters is studied. This identifies those properties of the single determinantal wave function that are essential for the method, thus providing the mathematical foundation for extending the method to more general cases like multiconfigurational (Deumens *et al.*, 1991) wave functions and other groups (Deumens *et al.*, 1987a, 1987b). The general theory of coherent states can be found, for example, in the works by Perelomov (1972, 1986) and Kramer and Saraceno (1981), and in the review by Klauder and Skagerstam (1985).

Coherent states were first used by Glauber (Klauder and Skagerstam, 1985) to study the coherence of photons in laser beams. The mathematical properties of the wave functions used by Glauber were then generalized. The definition of a "generalized" coherent states is as follows: Let $|z\rangle$ be a state depending on one or more real or complex parameters z such that (1) $|z\rangle$ is a continuous function of z, and (2) a measure $d\mu(z)$ exists on the parameter space such that the identity operator in Hilbert space can be represented as

$$I=\int |z\rangle\langle z| d\mu(z) . \tag{2.30}$$

The mathematical property that all projectors $|z\rangle\langle z|$ add up (coherently) to the unit operator is what distinguishes coherent states from any overcomplete set of states with a continuous label. It is by no means a simple matter to show for a given parametrized set that the resolution of the identity holds.

It was Perelomov (1972) who developed the systematic theory for constructing coherent states. He shows that given a Lie group G and a unitary representation T of that group in Hilbert space, it is possible to construct a family of states that have the properties required of coherent states. Let H be a subgroup of G that leaves the state $|\Psi_0\rangle$ invariant, i.e., for all elements h of H

$$T(h)|\Psi_0\rangle=|\Psi_0\rangle ; \tag{2.31}$$

then the coherent state is

$$|z\rangle=T(g)|\Psi_0\rangle=T(c)T(h)|\Psi_0\rangle=T(c)|\Psi_0\rangle , \tag{2.32}$$

where z is the element of the coset space G/H corresponding to g of G.

The discussion of the single determinant as a coherent state is presented in detail by Kramer and Saraceno (1981) and by Perelomov in his book (Perelomov, 1986). The coherent-state formulation of a determinantal wave function is based on the Thouless representation (Thouless, 1960). The Lie group G is the unitary group $U(K)$ of single-particle transformations. In principle, one should consider the infinite-dimensional single-particle space, but K is assumed to be finite.

The reference state (2.22) is a lowest weight state for the irreducible representation $[1^N 0^{(K-N)}]$ of the group $\mathrm{U}(K)$ with generators $b_i^\dagger b_j$, because the weight operators $b_i^\dagger b_i$ acting on the reference state have eigenvalue 1 for $i=1,\ldots,N$, and 0 for $i=N+1,\ldots,K$. The stability group of the reference state is $\mathrm{U}(N)\times\mathrm{U}(K-N)$. This only expresses the well-known invariance of a determinantal wave function to the transformation of the occupied spin-orbitals among themselves and the unoccupied among themselves. A complex parametrization of the coset space $\mathrm{U}(K)/\mathrm{U}(N)\times\mathrm{U}(K-N)$ is introduced by using the following decomposition of the elements of $\mathrm{U}(K)$. Extending the group $\mathrm{U}(K)$ first to $\mathrm{GL}(K,\mathbf{C})$, one obtains the right coset decomposition $g=ch$ of an element g of $\mathrm{U}(K)$ where c is a coset representative and where h is an element of the stability group $\mathrm{U}(N)\times\mathrm{U}(K-N)$.[2]

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[2] The left coset decomposition is obtained in a similar way. Kramer and Saraceno use it because they define the coherent state in a nonstandard way.

Next, the Gauss factorization of an arbitrary group element is introduced,

$$c=\begin{bmatrix} I^{\bullet} & 0 \\ z & I^{\circ} \end{bmatrix}\begin{bmatrix} x^{\bullet} & 0 \\ 0 & x^{\circ} \end{bmatrix}\begin{bmatrix} I^{\bullet} & y^{\dagger} \\ 0 & I^{\circ} \end{bmatrix} . \tag{2.33}$$

This leads to a parametrization of the coset space in terms of the complex parameters z, with x and y determined as functions of z from the condition that c be unitary. Multiplying the matrix factors of c, one gets

$$c=\begin{bmatrix} x^{\bullet} & x^{\bullet}y^{\dagger} \\ zx^{\bullet} & zx^{\bullet}y^{\dagger}+x^{\circ} \end{bmatrix} , \tag{2.34}$$

and hence the unitarity implies

$$\begin{aligned} c^{\dagger}c&=\begin{bmatrix} I^{\bullet} & 0 \\ 0 & I^{\circ} \end{bmatrix} \\ &=\begin{bmatrix} x^{\bullet\dagger}(I^{\bullet}+z^{\dagger}z)x^{\bullet} & x^{\bullet\dagger}(x^{\bullet}y^{\dagger}+z^{\dagger}zx^{\bullet}y^{\dagger}+z^{\dagger}x^{\circ}) \\ (yx^{\bullet\dagger}+yx^{\bullet\dagger}z^{\dagger}z+x^{\circ\dagger}z)x^{\bullet} & yx^{\bullet\dagger}x^{\bullet}y^{\dagger}+yx^{\bullet\dagger}z^{\dagger}zx^{\bullet}y^{\dagger}+yx^{\bullet\dagger}z^{\dagger}x^{\circ}+x^{\circ\dagger}zx^{\bullet}y^{\dagger}+x^{\circ\dagger}x^{\circ} \end{bmatrix} . \end{aligned} \tag{2.35}$$

This yields

$$x^{\bullet}=(I^{\bullet}+z^{\dagger}z)^{-1/2} \tag{2.36}$$

and

$$yx^{\bullet\dagger}=-x^{\circ\dagger}z(I^{\bullet}+z^{\dagger}z)^{-1} \tag{2.37}$$

from the first column of the matrix equation. Using the last equation for y, the upper diagonal equation gives

$$x^{\circ}=(I^{\circ}+zz^{\dagger})^{1/2} \tag{2.38}$$

where Eq. (2.28) is used, and

$$y=-(I^{\circ}+zz^{\dagger})^{1/2}z(I^{\bullet}+z^{\dagger}z)^{-1/2} . \tag{2.39}$$

Let T be the appropriate unitary irreducible representation of U(K) in Fermi-Fock space. An arbitrary single-determinantal state with occupied orbitals $\chi^{\bullet}$ is defined by selecting a set of occupied creators from the general set given in Eq. (2.20),

$$c^{\bullet\dagger}=(b^{\bullet\dagger}\ \ b^{\circ\dagger})\begin{bmatrix} U^{\bullet} & U^{>} \\ U^{\vee} & U^{\circ} \end{bmatrix}\begin{bmatrix} I^{\bullet} \\ 0 \end{bmatrix} .$$

The unitary representation is defined to act on the coefficients, rather than on the basis functions or the field operators $b^{\dagger}$ as

$$\begin{aligned} T(g)|\Psi\rangle&=T(g)|c^{\bullet\dagger}\rangle \\ &=T(g)\left|b^{\dagger}U\begin{bmatrix} I^{\bullet} \\ 0 \end{bmatrix}\right\rangle\equiv\left|b^{\dagger}gU\begin{bmatrix} I^{\bullet} \\ 0 \end{bmatrix}\right\rangle . \end{aligned} \tag{2.40}$$

This is in accordance with the active point of view of coordinate transformations.

The coherent state is then defined, following Perelomov (1972), as

$$\begin{aligned} |\Psi\rangle&=T(ch)|\Psi_0\rangle=T(ch)|b^{\bullet\dagger}\rangle \\ &=\left|b^{\dagger}ch\begin{bmatrix} I^{\bullet} \\ 0 \end{bmatrix}\right\rangle \\ &=\left|b^{\dagger}\begin{bmatrix} I^{\bullet} & 0 \\ z & I^{\circ} \end{bmatrix}\begin{bmatrix} x^{\bullet} & 0 \\ 0 & x^{\circ} \end{bmatrix}\begin{bmatrix} I^{\bullet} & y^{\dagger} \\ 0 & I^{\circ} \end{bmatrix}\begin{bmatrix} I^{\bullet} \\ 0 \end{bmatrix}\right\rangle \\ &=\alpha\left|b^{\dagger}\begin{bmatrix} I^{\bullet} & 0 \\ z & I^{\circ} \end{bmatrix}\begin{bmatrix} I^{\bullet} \\ 0 \end{bmatrix}\right\rangle \\ &=\alpha\prod_{h=1}^{N}\left[b_h^{\bullet\dagger}+\sum_{p=N+1}^{K}b_p^{\circ\dagger}z_{ph}\right]|\mathrm{vac}\rangle \\ &=\alpha\exp\left[\sum_{h=1}^{N}\sum_{p=N+1}^{K}z_{ph}b_p^{\circ\dagger}b_h^{\bullet}\right]|\Psi_0\rangle . \end{aligned} \tag{2.41}$$

The second step uses the fact that h is in the stability group of the reference state, and the next step that the rightmost factor of c in Eq. (2.33) modifies only the virtual space and leaves the reference state unaffected while the middle factor of c only gives a constant α when acting on the reference state. The constant α is determined from the normalization of the coherent state. In the following the un-normalized coherent state

$$\begin{aligned} |z\rangle&=\exp\left[\sum_{h=1}^{N}\sum_{p=N+1}^{K}z_{ph}b_p^{\circ\dagger}b_h^{\bullet}\right]|\Psi_0\rangle \\ &=\prod_{h=1}^{N}\left[b_h^{\bullet\dagger}+\sum_{p=N+1}^{K}b_p^{\circ\dagger}z_{ph}\right]|\mathrm{vac}\rangle \end{aligned} \tag{2.42}$$

is used. This is recognized as the Thouless representation (2.20) of a determinantal wave function with the elements of the $(K-N)\times N$ matrix z as time-dependent parameters.

Because this is a coherent state, Eq. (2.30) holds with the measure given by

$$d\mu(z)\propto\det(I^{\bullet}+z^{\dagger}z)^{-K}\prod_{(ph)=1}^{N(K-N)}d(\mathrm{Re}z_{ph})d(\mathrm{Im}z_{ph}) , \tag{2.43}$$

where the results of Lemma 2 on p. 138 in Perelomov's (1986) book have been used.

C. Treatment of the nuclei

The two extremes for treatment of the nuclei are, on the one hand, classical point particles and, on the other, properly symmetrized many-nuclei wave functions represented on a grid. Using a mixture of classical parameters and superpositions of nuclear wave packets, one can construct a treatment that is general enough to encompass both and to permit some insight into nuclear dynamics. It provides a recipe for simplifying a given treatment when less accuracy is desired or computational resources are insufficient.

It can be shown that the eikonal approximation (Mott and Massey, 1965) leads to classical trajectory equations for the nuclei. Combining the eikonal approximation with time correlation functions (Villalonga and Micha, 1992) makes it possible to readily calculate double-differential cross sections. Heller (1975) also devices classical trajectory equations from the assumption of frozen Gaussian wave packets. The additional degree of freedom of thawed Gaussian wave packets, which allows their width to change dynamically, seems to cause more problems than it solves (Reimers and Heller, 1988). A more general approach is to introduce time-dependent basis sets (Kučar and Meyer, 1989). There are certain processes where it is essential to have the capability for nuclear wave packets to split in a correlated way (Hammerich *et al.*, 1990). The general description with multiconfigurational wave functions has been studied in the framework of time-dependent treatments (Hammerich *et al.*, 1990; Meyer *et al.*, 1990; Deumens *et al.*, 1991) and can be applied for electronic and nuclear degrees of freedom without fundamental problems. It is beyond the scope of this review to explore the details, although it should clearly be acknowledged that there are problems, the very nature of which require a multiconfigurational treatment.

In the derivation below, classical nuclei are used. This description is sufficient for many problems and, together with the single-determinantal representation of the electrons, results in an attractively simple model. The nuclear parameters at this level of treatment are the positions $R=\{\mathbf{R}_k\}_k$ and momenta $P=\{\mathbf{P}_k\}_k$. It is sometimes useful to think of classical nuclei as the limit of narrow Gaussian wave packets. The nuclear one-particle functions are given by (Deumens, Diz, Taylor, and Öhrn, 1992)

$$\exp\left[-a(\mathbf{X}-\mathbf{R}_k)^2+\frac{i}{\hbar}\mathbf{P}_k\cdot\mathbf{X}\right]\propto\exp[-a(\mathbf{X}-\mathbf{Z}_k)^2] \tag{2.44}$$

with expectation value $\mathbf{R}_k$ for the nuclear position operator $\mathbf{X}$, $\mathbf{P}_k$ for the nuclear momentum operator $-i\hbar\nabla_{\mathbf{X}}$, and $\mathbf{Z}_k=(\mathbf{R}_k+i\mathbf{P}_k/2a\hbar)/\sqrt{2}$. The classical treatment of the nuclei can be viewed as taking the limits $\hbar\to 0, a\to\infty$ with $2\hbar a\to 1$ of many-nuclei wave functions constructed with Gaussian wave packets.

As pointed out by Delos (1981), the treatment with semiclassical nuclei exhibits all characteristics of the full quantum treatment. The discussion below can be extended to a fully quantum-mechanical treatment with minimal theoretical—but significant computational—effort, for example, by introducing a moving basis of nuclear functions as done by Kučar and Meyer (1989).

D. The time-dependent variational principle

Given the parametrized state $|\zeta\rangle$ with the appropriate form of wave function, the time-dependent variational principle (Kramer and Saraceno, 1981) is used to obtain dynamical equations for the $2N(K-N)+2N_{\text{at}}$ complex parameters ζ

$$\{\zeta_\alpha\}_\alpha=\{z_{ph},Z_{ik}\}_{phik} \ . \tag{2.45}$$

Here z are, for instance, the Thouless parameters for electrons, and Z are complex nuclear parameters defined in terms of nuclear coordinates R and momenta P as

$$\mathbf{Z}_k=\frac{1}{\sqrt{2}}(\mathbf{R}_k+i\mathbf{P}_k) \ . \tag{2.46}$$

Although any wave function dependent on a set of parameters can be used in the TDVP, the determinantal state results in simple, well-structured equations, as can be seen from the details in this paper.

It is not important for all applications that the overall phase of the wave packet be correct. However, in some cases, such as for autocorrelation functions, it is essential (Löwdin and Mukherjee, 1972). The phase factor can be obtained by including among the parameters a complex factor $\alpha=N\exp(i\gamma)$ multiplying the wave function. The TDVP employed here is norm independent, which leads to a straightforward derivation of the dynamical equations.

The TDVP starts from the variation of the quantum-mechanical action A,

$$\delta A=\delta\int\left[\frac{i}{2}\left[\langle\zeta|\frac{d}{dt}(|\zeta\rangle)-\frac{d}{dt}(\langle\zeta|)|\zeta\rangle\right]-\langle\zeta|H|\zeta\rangle\right]\langle\zeta|\zeta\rangle^{-1}dt=0 \ . \tag{2.47}$$

Defining the "left acting derivative" as

$$f\frac{\tilde{d}}{dt}=\frac{d}{dt}f \ , \tag{2.48}$$

introducing the operator

$$\Theta=\frac{i}{2}\left[\frac{d}{dt}-\frac{\tilde{d}}{dt}\right]-H \ , \tag{2.49}$$

and then using integration by parts with the appropriate boundary conditions, one can write

$$\begin{aligned}\delta A&=\delta\int\langle\xi|\Theta|\xi\rangle\langle\xi|\xi\rangle^{-1}dt=0\\&=\int\left[\langle\delta\xi|i\frac{d}{dt}|\xi\rangle-\langle\delta\xi|H|\xi\rangle-\langle\xi|\Theta|\xi\rangle\langle\xi|\xi\rangle^{-1}\langle\delta\xi|\xi\rangle+\text{c.c.}\right]\langle\xi|\xi\rangle^{-1}dt\ .\end{aligned}\tag{2.50}$$

Considering first completely general variations, the time-dependent state must satisfy

$$\left[i\hbar\frac{d}{dt}-H\right]|\xi\rangle=\frac{\langle\xi|\Theta|\xi\rangle}{\langle\xi|\xi\rangle}|\xi\rangle\ .\tag{2.51}$$

This is the Schrödinger equation, provided the right-hand side is zero. One can achieve this by explicitly considering the phase factor, i.e.,

$$\begin{gathered}\langle\xi|e^{-i\gamma}\Theta e^{i\gamma}|\xi\rangle=0\ ,\\\langle\xi|e^{-i\gamma}\tfrac{1}{2}(i(i\dot\gamma)-i(-i\dot\gamma))e^{i\gamma}|\xi\rangle+\langle\xi|\Theta|\xi\rangle=0\ ,\\-\langle\xi|\xi\rangle\dot\gamma+\langle\xi|\Theta|\xi\rangle=0\ ,\\\dot\gamma=\frac{\langle\xi|\Theta|\xi\rangle}{\langle\xi|\xi\rangle}\ .\end{gathered}\tag{2.52}$$

Writing the quantum state $|\xi\rangle$ as a wave function, $\Psi(\mathbf{r},\mathbf{R},t)=\langle\mathbf{r},\mathbf{R}|\xi\rangle$, and including the phase factor to get $\Phi(\mathbf{r},\mathbf{R},t)=e^{i\gamma}\Psi(\mathbf{r},\mathbf{R},t)$, recovers the Schrödinger equation,

$$\left[i\frac{\partial}{\partial t}-H\right]\Phi(\mathbf{r},\mathbf{R},t)=0\ ,\tag{2.53}$$

where the total time derivative in the bra-ket formulation is changed to a partial time derivative.

Introducing the notations

$$\begin{aligned}&S(\xi^*,\xi)=\langle\xi|\xi\rangle\ ,\\&E(\xi^*,\xi)=\langle\xi|H|\xi\rangle/\langle\xi|\xi\rangle\ ,\end{aligned}\tag{2.54}$$

one can write

$$\begin{aligned}\dot\gamma&=\frac{i}{2}\sum_\alpha\left[\dot\xi_\alpha\frac{\partial\ln S(\xi^*,\xi)}{\partial\xi_\alpha}-\dot\xi^*_\alpha\frac{\partial\ln S(\xi^*,\xi)}{\partial\xi^*_\alpha}\right]-E(\xi^*,\xi)\\&=-\mathrm{Im}\left[\sum_\alpha\dot\xi_\alpha\frac{\partial\ln S(\xi^*,\xi)}{\partial\xi_\alpha}\right]-E(\xi^*,\xi)\ .\end{aligned}\tag{2.55}$$

This differential equation can be integrated with a simple quadrature.

Next, consider only variations induced by parameter changes in the approximate state vector. Because all time dependence of the coherent state is through the parameters, Eq. (2.47) is equivalent to

$$\begin{aligned}\delta A&=\delta\int\left[\frac{i}{2}\sum_\alpha\left[\dot\xi_\alpha\frac{\partial}{\partial\xi_\alpha}-\dot\xi^*_\alpha\frac{\partial}{\partial\xi^*_\alpha}\right]\ln S-E\right]dt\\&=\int\left[i\sum_{\alpha,\beta}\left[\frac{\partial^2\ln S}{\partial\xi_\alpha\partial\xi^*_\beta}\dot\xi_\alpha\delta\xi^*_\beta-\frac{\partial^2\ln S}{\partial\xi^*_\alpha\partial\xi_\beta}\dot\xi^*_\alpha\delta\xi_\beta\right]-\delta E\right]dt\\&=\int\sum_\beta\left[\left[-i\sum_\alpha\frac{\partial^2\ln S}{\partial\xi^*_\alpha\partial\xi_\beta}\dot\xi^*_\alpha-\frac{\partial E}{\partial\xi_\beta}\right]\delta\xi_\beta+\left[i\sum_\alpha\frac{\partial^2\ln S}{\partial\xi_\alpha\partial\xi^*_\beta}\dot\xi_\alpha-\frac{\partial E}{\partial\xi^*_\beta}\right]\delta\xi^*_\beta\right]dt\ .\end{aligned}\tag{2.56}$$

The second step in Eq. (2.56) involves a partial integration of some terms with respect to t. Since all the $\delta\xi$ and their complex conjugates are independent variations, the dynamical equations become

$$\begin{aligned}&i\sum_\beta C_{\alpha\beta}\dot\xi_\beta=\frac{\partial E}{\partial\xi^*_\alpha}\ ,\\&-i\sum_\beta C^*_{\alpha\beta}\dot\xi^*_\beta=\frac{\partial E}{\partial\xi_\alpha}\ ,\end{aligned}\tag{2.57}$$

with the elements of the Hermitian metric matrix C defined as

$$C_{\alpha\beta}=\frac{\partial^2\ln S}{\partial\xi^*_\alpha\partial\xi_\beta}\ .\tag{2.58}$$

Note that the phase factor does not influence the evolution of the other parameters, so it can be computed separately. In practice, however, it is convenient to integrate (2.55) along with Eqs. (2.57) for the other parameters.

Equations (2.57) can be written in matrix form as

$$i\begin{bmatrix}C&0\\0&-C^*\end{bmatrix}\begin{bmatrix}\dot\xi\\\dot\xi^*\end{bmatrix}=\begin{bmatrix}\dfrac{\partial E}{\partial\xi^*}\\\dfrac{\partial E}{\partial\xi}\end{bmatrix}\ .\tag{2.59}$$

Furthermore, a generalized Poisson bracket $\{,\}$ is defined for two functions f and g depending on ξ and ξ^* as

$$\{f,g\}=\begin{bmatrix}\dfrac{\partial f}{\partial\xi^{\mathrm{T}}}&\dfrac{\partial f}{\partial\xi^{\dagger}}\end{bmatrix}\begin{bmatrix}-iC^{-1}&0\\0&iC^{*-1}\end{bmatrix}\begin{bmatrix}\dfrac{\partial g}{\partial\xi^*}\\\dfrac{\partial g}{\partial\xi}\end{bmatrix}\ .\tag{2.60}$$

With the symplectic structure defined by this Poisson bracket, the Schrödinger equation restricted to the set of parametrized states becomes a classical Hamiltonian system; i.e., the evolution equations (2.57) assume the standard form

$$\dot{\zeta}=\{\zeta,E\}, \quad \dot{\zeta}^{*}=\{\zeta^{*},E\} \ . \tag{2.61}$$

Parameters ζ and ζ^* are conjugate variables, as illustrated by the relations

$$\{\zeta,\zeta\}=0, \quad \{\zeta^{*},\zeta^{*}\}=0, \quad \{\zeta,\zeta^{*}\}=-iC^{-1} \ . \tag{2.62}$$

Defining real coordinates p and q such that $\zeta=(q+ip)/\sqrt{2}$ and the symmetric matrix $A=\mathrm{Im}(C^{-1})$ and the antisymmetric matrix $B=\mathrm{Re}(C^{-1})$, we can write the Poisson bracket in the more familiar real form,

$$\{f,g\}=\begin{bmatrix} \dfrac{\partial f}{\partial q^{\mathrm{T}}} & \dfrac{\partial f}{\partial p^{\mathrm{T}}} \end{bmatrix} \begin{bmatrix} A & B \\ -B & A \end{bmatrix} \begin{bmatrix} \dfrac{\partial g}{\partial q} \\ \dfrac{\partial g}{\partial p} \end{bmatrix} \ . \tag{2.63}$$

The matrices

$$M=\begin{bmatrix} -iC^{-1} & 0 \\ 0 & iC^{*-1} \end{bmatrix} \tag{2.64}$$

and

$$\begin{bmatrix} A & B \\ -B & A \end{bmatrix} \tag{2.65}$$

define the symplectic structure of the phase space (Abraham and Marsden, 1978). A transformation that leaves the geometric structure of the phase space—the symplectic structure—invariant is called a symplectic transformation (Abraham and Marsden, 1978). In a flat phase space it is always possible to find a global coordinate system such that the symplectic form takes on the familiar form (Goldstein, 1980)

$$J=\begin{bmatrix} 0 & I \\ -I & 0 \end{bmatrix} \ . \tag{2.66}$$

All symplectic transformations form the familiar group $\mathrm{Sp}(2N(K-N)+2N_{\mathrm{at}},\mathbf{R})$ of matrix transformations that leave J invariant. However, in a curved phase space the transformation to the constant form J is possible only on a local coordinate chart (see Darboux's theorem in Abraham and Marsden, 1978). It is generally not a trivial matter to construct this transformation.

III. ELECTRON-NUCLEAR DYNAMICS

A. Orthonormal representation

The dynamical equations in an orthonormal basis fixed in space are derived in this section. Although this is an ill-advised basis for computations, its mathematical simplicity makes it a convenient starting point. It is then easy to derive the much more useful, and more familiar, equations in an orthonormal basis built from the usual atomic orbitals that follow the nuclei. It is our experience that the fixed basis is a worthwhile detour to make in order to understand properly the structure of the equations. Furthermore, it is the physically meaningful basis for applications in extended systems (Theilhaber, 1992).

Although the precise form of the orthonormal basis is irrelevant for the derivation, it may be useful to think of a definite basis. A good example is the three-dimensional oscillator eigenfunctions. Another choice for which completeness is harder to prove but that has more physical appeal would be a set of molecular orbitals built from atomic orbitals centered at the initial positions of the nuclei. An appropriate definition of molecular orbitals is the set of orbitals that diagonalizes the Fock matrix, because the single-determinantal wave function has a simple description in that basis. Obviously, as the nuclei move, the description of the electronic wave function will rely more and more on the completeness of the fixed basis; but that presents no problem, in principle.

Next, the dynamical equations are developed in an orthonormal basis built with traveling atomic orbitals. It is noteworthy that this can be done by a phase-space coordinate transformation of the equations developed for a space-fixed basis to new independent dynamical variables. The resulting equations are a generalization of the ones used by Field (1992).

1. Representation in an orthonormal basis fixed in space

The *ab initio* molecular Hamiltonian written in second quantization in an orthonormal molecular basis is

$$H=\sum_{k=1}^{N_{\mathrm{at}}} \frac{\mathbf{P}_k^2}{2M_k}+\sum_{\substack{k,l=1\\k<l}}^{N_{\mathrm{at}}} \frac{Z_k Z_l e^2}{|\mathbf{R}_k-\mathbf{R}_l|} + \sum_{i,j=1}^{K} h_{ij} b_i^{\dagger} b_j + \frac{1}{4} \sum_{i,j,k,l=1}^{K} V_{ij;kl} b_i^{\dagger} b_j^{\dagger} b_l b_k \ . \tag{3.1}$$

The symbols h and V denote the one-electron (Z_k is here the atomic number of nucleus k)

$$h_{ij}=\int \psi_i^{*}(\mathbf{r}) \left[-\frac{\hbar^2}{2m}\nabla^2 - \sum_{k=1}^{N_{\mathrm{at}}} \frac{Z_k e^2}{|\mathbf{r}-\mathbf{R}_k|} \right] \psi_j(\mathbf{r}) d^3 r \tag{3.2}$$

and antisymmetrized two-electron integrals

$$V_{ij;kl}=\langle ij \| kl \rangle = \langle ij | kl \rangle - \langle ij | lk \rangle \ , \tag{3.3}$$

with

$$\langle ij | kl \rangle = e^2 \int \frac{\psi_i^{*}(\mathbf{r}_1)\psi_j^{*}(\mathbf{r}_2)\psi_k(\mathbf{r}_1)\psi_l(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} d^3 r_1 d^3 r_2 \ , \tag{3.4}$$

in the molecular two-component spin-orbital basis. The one-electron integrals form a Hermitian matrix. The two-electron integrals have the following symmetries:

$$\begin{aligned}\langle ij|kl\rangle &= \langle ji|lk\rangle \\ &= \langle kl|ij\rangle^* = \langle lk|ji\rangle^* \, . \end{aligned} \tag{3.5}$$

When real atomic orbitals are used, there are the additional symmetries

$$\begin{aligned}\langle ij|kl\rangle &= \langle ji|lk\rangle \\ &= \langle kl|ij\rangle = \langle lk|ji\rangle \\ &= \langle kj|il\rangle = \langle jk|li\rangle \\ &= \langle il|kj\rangle = \langle li|jk\rangle \, . \end{aligned} \tag{3.6}$$

The overlap S_{el} of two single-determinantal wave functions of the form defined in Sec. II.B is easily obtained,

$$\begin{aligned} S_{\mathrm{el}}(z'^*z) &= \langle z'|z\rangle \\ &= \langle \mathrm{vac}| \prod_{g=1}^{N} c_g^{\bullet}(z') \prod_{h=1}^{N} c_h^{\bullet\dagger}(z)|\mathrm{vac}\rangle \\ &= \det\left[\left\{\left\langle \psi_g^{\bullet} + \sum_{q=N+1}^{K} \psi_q^{\circ} z'_{qg} \middle| \psi_h^{\bullet} + \sum_{p=N+1}^{K} \psi_p^{\circ} z_{ph}\right\rangle\right\}_{gh}\right] \\ &= \det\left[\left\{\delta_{gh} + \sum_{p=N+1}^{K} z'^*_{pg} z_{ph}\right\}_{gh}\right] \\ &= \det(I^{\bullet} + z'^{\dagger} z) \, . \end{aligned} \tag{3.7}$$

Note from this equation that the norm of a single-determinantal wave function is not unity in the Thouless parametrization. This is a direct consequence of requiring that the state be an analytic function of the z parameters.

To evaluate the energy and its derivatives, the one-particle density matrix, or one-matrix, is needed, which is defined as

$$\Gamma_{ij} = \langle z|z\rangle^{-1}\langle z|b_j^{\dagger} b_i|z\rangle \tag{3.8}$$

and has the block form

$$\Gamma = \begin{bmatrix} \Gamma^{\bullet} & \Gamma^{>} \\ \Gamma^{\vee} & \Gamma^{\circ} \end{bmatrix} \, . \tag{3.9}$$

The two-particle density matrix, or two-matrix, for a single-determinantal wave function is a simple function of the one-matrix (Linderberg and Öhrn, 1973)

$$\Gamma^{(2)}_{ij,kl} = \langle z|z\rangle^{-1}\langle z|b_i^{\dagger} b_j^{\dagger} b_l b_k|z\rangle = \Gamma_{ki}\Gamma_{lj} - \Gamma_{kj}\Gamma_{li} \, . \tag{3.10}$$

The explicit forms of the matrix elements of the one-matrix as functions of the z parameters are given by Eq. (A21) and are derived in Sec. 1.b in the Appendix.

The molecular energy includes the classical nuclear kinetic and internuclear repulsion energy

$$E^{(0)} = \sum_{k=1}^{N_{\mathrm{at}}} \frac{\mathbf{P}_k^2}{2M_k} + \sum_{\substack{k,l=1 \\ k<l}}^{N_{\mathrm{at}}} \frac{Z_k Z_l e^2}{|\mathbf{R}_k - \mathbf{R}_l|} \, . \tag{3.11}$$

When the nuclei are treated quantum mechanically, this term has to be replaced with the expectation value in the appropriate nuclear state. The energy of the molecular state can be expressed as

$$\begin{aligned} E(z^*,z,R,P) &= E^{(0)} + \mathrm{Tr}(h\Gamma) + \frac{1}{4}\mathrm{Tr}(V\Gamma^{(2)}) \\ &= E^{(0)} + \mathrm{Tr}(h\Gamma) + \frac{1}{4}\mathrm{Tr}[\mathrm{Tr}(V_{ab;ab}\Gamma)_a\Gamma]_b - \frac{1}{4}\mathrm{Tr}[\mathrm{Tr}(V_{ab;ba}\Gamma)_a\Gamma]_b \\ &= E^{(0)} + \mathrm{Tr}(h\Gamma) + \frac{1}{2}\mathrm{Tr}[\mathrm{Tr}(V_{ab;ab}\Gamma)_a\Gamma]_b \\ &= E^{(0)} + E^{(1)} + E^{(2)} \, , \end{aligned} \tag{3.12}$$

where the notation

$$\mathrm{Tr}(V_{ab;ab}M)_a = \sum_{i,j} V_{ik;jl} M_{ji} \tag{3.13}$$

is used for partial traces involving the four-index object V of two-electron integrals.

The action for a classical dynamical system with a Hamiltonian function $E(R,P)$ is varied to yield

$$
\begin{aligned}
\delta A &= \delta \int \left[\frac{1}{2} \sum (\mathbf{P}_k \cdot \dot{\mathbf{R}}_k - \dot{\mathbf{P}}_k \cdot \mathbf{R}_k) - E \right] dt \\
&= \int \sum [\tfrac{1}{2} \delta \mathbf{P}_k \cdot \dot{\mathbf{R}}_k + \tfrac{1}{2} \mathbf{P}_k \cdot \delta \dot{\mathbf{R}}_k - \tfrac{1}{2} \delta \dot{\mathbf{P}}_k \cdot \mathbf{R}_k - \tfrac{1}{2} \dot{\mathbf{P}}_k \cdot \delta \mathbf{R}_k - \nabla_{\mathbf{R}_k} E \cdot \delta \mathbf{R}_k - \nabla_{\mathbf{P}_k} E \cdot \delta \mathbf{P}_k] dt \\
&= \int \sum [(\dot{\mathbf{R}}_k - \nabla_{\mathbf{P}_k} E) \cdot \delta \mathbf{P}_k - (\dot{\mathbf{P}}_k + \nabla_{\mathbf{R}_k} E) \cdot \delta \mathbf{R}_k] dt = 0 \ ,
\end{aligned}
\tag{3.14}
$$

where partial integration, as before, has been performed on some terms. This yields the well-known classical equations of Hamilton.

The following properties of the complex form of the nuclear coordinates, using Eq. (2.46), are important in developing the system of coupled equations for a molecular system in which the nuclei are treated as classical particles,

$$
\begin{aligned}
\frac{1}{2}(\mathbf{P}_k \cdot \dot{\mathbf{R}}_k - \dot{\mathbf{P}}_k \cdot \mathbf{R}_k) &= \frac{i}{2}(\mathbf{Z}_k^* \cdot \dot{\mathbf{Z}}_k - \dot{\mathbf{Z}}_k^* \cdot \mathbf{Z}_k) \\
&= \frac{i}{2}(\dot{\mathbf{Z}}_k \cdot \nabla_{\mathbf{Z}_k} - \dot{\mathbf{Z}}_k^* \cdot \nabla_{\mathbf{Z}_k'^*} |_{Z'=Z}) \left[\sum_l \mathbf{Z}_l'^* \cdot \mathbf{Z}_l \right] \\
&= \frac{i}{2}(\dot{\mathbf{Z}}_k \cdot \nabla_{\mathbf{Z}_k} - \dot{\mathbf{Z}}_k^* \cdot \nabla_{\mathbf{Z}_k'^*} |_{Z'=Z}) \ln S_{\mathrm{cl}}(Z'^*, Z) \ .
\end{aligned}
\tag{3.15}
$$

The mathematical construct S_{cl} is defined as

$$
S_{\mathrm{cl}}(Z'^*, Z) = \exp \left[\sum_l \mathbf{Z}_l'^* \cdot \mathbf{Z}_l \right] \ . \tag{3.16}
$$

As for the electrons, this overlap is not normalized to 1.

The total overlap is defined as the product

$$
S(\zeta'^*, \zeta) = S_{\mathrm{el}}(z'^*, z) S_{\mathrm{cl}}(Z'^*, Z) \ ,
$$

and the energy in Eq. (2.54) is expressed as

$$
E(\zeta^*, \zeta) = E(z^*, z, R, P) = E^{(0)}(Z^*, Z) + E_{\mathrm{el}}(z^*, Z^*, z, Z) \ , \tag{3.17}
$$

where the electronic part of the energy $E_{\mathrm{el}} = E^{(1)} + E^{(2)}$ depends on the real part of the nuclear parameters Z through the electron-nuclear attraction term. With these definitions the derivation of the dynamic equations for classical nuclei and electrons described by a single determinant is straightforward from the results of Sec. II.D and Eqs. (2.54)–(2.58). The system, Eq. (2.57), for z and Z in matrix form becomes

$$
\begin{bmatrix} iC & 0 & 0 & 0 \\ 0 & iI & 0 & 0 \\ 0 & 0 & -iC^* & 0 \\ 0 & 0 & 0 & -iI \end{bmatrix}
\begin{bmatrix} \dot{z} \\ \dot{Z} \\ \dot{z}^* \\ \dot{Z}^* \end{bmatrix}
=
\begin{bmatrix} \partial E / \partial z^* \\ \partial E / \partial Z^* \\ \partial E / \partial z \\ \partial E / \partial Z \end{bmatrix} , \tag{3.18}
$$

where the unit matrix comes from S_{cl}. Using the real form of the nuclear coordinates, we may express this as

$$
\begin{bmatrix} iC & 0 & 0 & 0 \\ 0 & -iC^* & 0 & 0 \\ 0 & 0 & 0 & -I \\ 0 & 0 & I & 0 \end{bmatrix}
\begin{bmatrix} \dot{z} \\ \dot{z}^* \\ \dot{R} \\ \dot{P} \end{bmatrix}
=
\begin{bmatrix} \partial E / \partial z^* \\ \partial E / \partial z \\ \partial E / \partial R \\ \partial E / \partial P \end{bmatrix} . \tag{3.19}
$$

The corresponding phase equation (2.55) is

$$
\dot{\gamma} = -\mathrm{Im} \left[\mathrm{Tr} \left[\dot{z} \frac{\partial \ln S_{\mathrm{el}}(z^*, z)}{\partial z} \right] \right] + \frac{1}{2} \sum_k (\mathbf{P}_k \cdot \dot{\mathbf{R}}_k - \dot{\mathbf{P}}_k \cdot \mathbf{R}_k) - E(z^*, z, R, P) \ . \tag{3.20}
$$

The electronic part of the metric, which is given by Eqs. (2.58) and (3.7), becomes (see Sec. 1.a in the Appendix for the derivation)

$$
C_{ph,qg} = [(I^{\bullet} + z^{\dagger} z)^{-1}]_{gh} [(I^{\circ} + z z^{\dagger})^{-1}]_{pq} \ , \tag{3.21}
$$

which can readily be inverted. The explicit expression of the energy derivatives as a function of the z parameters is given in Sec. 1.c in the Appendix. Since the energy derivative, Eq. (A29), contains the factors of C, the metric can be eliminated and the dynamical equations (3.19) become

$$
\begin{aligned}
i\dot{z} &= (-z \quad I^{\circ}) [h + \mathrm{Tr}(V_{ab;ab} \Gamma)_a] \begin{bmatrix} I^{\bullet} \\ z \end{bmatrix} \\
&= (-z \quad I^{\circ}) F \begin{bmatrix} I^{\bullet} \\ z \end{bmatrix} ,
\end{aligned}
\tag{3.22}
$$

where the Fock matrix F is defined as

$$
F = h + \mathrm{Tr}(V_{ab;ab} \Gamma)_a \ , \tag{3.23}
$$

and

$$
\begin{aligned}
\dot{\mathbf{P}}_k = \sum_{l \neq k} \frac{Z_k Z_l e^2 (\mathbf{R}_k - \mathbf{R}_l)}{|\mathbf{R}_k - \mathbf{R}_l|^3} - \mathrm{Tr}(\nabla_{\mathbf{R}_k} h \Gamma) \\
- \mathrm{Tr}[\mathrm{Tr}(\nabla_{\mathbf{R}_k} V_{ab;ab} \Gamma)_a \Gamma] \ ,
\end{aligned}
\tag{3.24}
$$

from Eq. (A30) and

$$\dot{\mathbf{R}}_k = \frac{\mathbf{P}_k}{M_k} \; . \tag{3.25}$$

Here again the partial trace notation of Eq. (3.13) has been used. The total phase satisfies (3.20), which becomes, using Eq. (A1),

$$\dot{\gamma} = -\operatorname{Im}\operatorname{Tr}[\dot{z}(I^{\bullet}+z^{\dagger}z)^{-1}z^{\dagger}] + \frac{1}{2}\sum_k (\mathbf{P}_k\cdot\dot{\mathbf{R}}_k - \dot{\mathbf{P}}_k\cdot\mathbf{R}_k) - E(z^*,z,R,P) \; . \tag{3.26}$$

Kulander and collaborators have implemented these equations for *ab initio* Hamiltonians using a representation of the electronic orbitals on a grid fixed in space (Tiszauer and Kulander, 1991). This form of the evolution equations is the Hartree-Fock-theory equivalent of the TDDF equations (1.11) derived by Theilhaber (1992). In TDDF one studies the dynamics of the nuclei in an extended system around equilibrium, and therefore it is sufficient to represent the electronic Kohn-Sham orbitals on a numerical grid fixed in space. The equations can be used equally successfully for studies of molecular vibrations.

2. Symplectic transformation to traveling atomic orbitals

The dynamical equations just obtained are convenient for theoretical derivations and for gaining insight. However, as stated before, from a numerical point of view, the use of molecular orbitals fixed in space leads to severe convergence problems as soon as the nuclei move away substantially from the region covered by the molecular orbitals. In this section a transformation is introduced in the generalized phase space of the dynamical system to new dynamical coordinates that preserves the structure of the dynamical equations. This transformation is a symplectic transformation because it preserves the symplectic structure of the phase space (Abraham and Marsden, 1978). To see that it is an element of the symplectic group $\mathrm{Sp}[2N(K-N)+2N_{\mathrm{at}},\mathbf{R}]$, i.e., that it preserves the symplectic form J of Eq. (2.66)—this is the coordinate-dependent definition of a symplectic transformation (Goldstein, 1980)—one first transforms to a coordinate system in which the symplectic structure takes on the form J. This expresses the equations in an orthonormal basis built with ordinary atomic orbitals that follows the nuclei, as is customary in electronic structure calculations, or in terms of traveling atomic orbitals, if electron translation factors are included.

First, the transformation from a nuclear basis built with fixed atomic orbitals to one built with traveling orbitals is considered. The transformation to a molecular basis built with the familiar atomic orbitals (AO's) that follow the nuclei but do not have electron translation factors (ETF's) can be obtained as a special case. One just deletes the P dependence and sets derivatives with respect to P equal to zero.

The transformation

$$\begin{bmatrix} z \\ Z \end{bmatrix} \rightarrow \begin{bmatrix} \tilde{z} \\ \tilde{Z} \end{bmatrix} , \tag{3.27}$$

or with the real form of the nuclear coordinates

$$\begin{bmatrix} z \\ R \\ P \end{bmatrix} \rightarrow \begin{bmatrix} \tilde{z} \\ \tilde{R} \\ \tilde{P} \end{bmatrix} , \tag{3.28}$$

leads to new independent dynamical variables $\tilde{z},\tilde{R},\tilde{P}$. Such a transformation will have the desired properties if the new nuclear coordinate axes are kept parallel to the old ones, i.e., $\tilde{R}=R$ and $\tilde{P}=P$, and the new electronic coordinates are allowed to acquire components along the original z,R,P.

When the parametrized states are expressed in terms of the molecular orbitals built with atomic orbitals centered on the nuclei, the calculation of the metric involves the overlap of two states with different nuclear geometries. If, furthermore, electron translation factors are included in the orbitals, the overlap also depends on the momenta of the nuclei, such that

$$S_{\mathrm{el}}(z'^*,R',P',z,R,P) = \det(\Delta^{\bullet}+\Delta^{>}z+z'^{\dagger}\Delta^{\vee}+z'^{\dagger}\Delta^{\circ}z) \; , \tag{3.29}$$

where the overlap matrix of the atomic basis $\Delta(R',P',R,P)$ depends on the nuclear positions and momenta. Note that the overlap matrix of two different bases is not Hermitian. It does become the unit matrix when the two nuclear configurations and momenta coincide, because the basis is then orthonormal. Because the TDVP is formulated with complex parameters and states that depend analytically on them, the calculus automatically keeps track of whether the derivative is taken with respect to the dependence through the bra or the ket in any expectation value. A more complex dependence on the nuclear positions and momenta occurs through the electronic orbitals. Indeed, since the orbitals depend on $\mathbf{R}_k$ and $\mathbf{P}_k$ separately and not through the complex combination $\mathbf{Z}_k$, the bra and ket both depend on $\mathbf{Z}_k$ and $\mathbf{Z}_k^*$. Because of this, one needs to keep track of the parameter dependence by differentiating with respect to unprimed and primed variables and setting them equal after differentiation. In order to simplify the formulas, the ket-gradient operators

$$\nabla_{\mathbf{R}_k}^{|\rangle} \langle R'|R\rangle \equiv \nabla_{\mathbf{R}_k} \langle R'|R\rangle |_{R'=R} \tag{3.30}$$

are introduced with obvious analogs for the bra-gradient and, similarly, for gradients with respect to nuclear momenta. The conventional gradient symbol $\nabla_{\mathbf{R}_k}$ denotes differentiation with respect to the full dependence, which can be made after the unprimed and primed variables have been set equal. An immediate consequence of the orthonormality of the basis is then

$$\nabla^{\langle|}_{\mathbf{R}_k}\Delta(R',R)+\nabla^{|\rangle}_{\mathbf{R}_k}\Delta(R',R)=\nabla_{\mathbf{R}_k}\Delta(R,R)=\nabla_{\mathbf{R}_k}I=0\ . \tag{3.31}$$

The transformation of the Poisson bracket uses the matrix of partial derivatives, or the Jacobian, T

$$\begin{bmatrix}\partial/\partial\tilde{z}^*\\ \partial/\partial\tilde{z}\\ \partial/\partial R\\ \partial/\partial P\end{bmatrix}=\begin{bmatrix}\partial z^*/\partial\tilde{z}^* & 0 & 0 & 0\\ 0 & \partial z/\partial\tilde{z} & 0 & 0\\ \partial z^*/\partial R & \partial z/\partial R & I & 0\\ \partial z^*/\partial P & \partial z/\partial P & 0 & I\end{bmatrix}\begin{bmatrix}\partial/\partial z^*\\ \partial/\partial z\\ \partial/\partial R\\ \partial/\partial P\end{bmatrix} \tag{3.32}$$

such that

$$T=\begin{bmatrix}c^* & 0 & 0 & 0\\ 0 & c & 0 & 0\\ r^* & r & I & 0\\ p^* & p & 0 & I\end{bmatrix}, \tag{3.33}$$

where $c=\partial z/\partial\tilde{z}$, $r=\partial z/\partial R$, and $p=\partial z/\partial P$. Using the fact that the inverse of a Jacobian is the Jacobian of the inverse transformation on the Poisson bracket, Eq. (2.60), yields the result

$$\begin{aligned}\{f,g\}&=\partial^\dagger f M^{-1}\partial g\\ &=\{f,g\}^{\sim}\\ &=\tilde{\partial}^\dagger f\tilde{M}^{-1}\tilde{\partial}g\\ &=\partial^\dagger f T^\dagger\tilde{M}^{-1}T\partial g\ ,\end{aligned} \tag{3.34}$$

so that the phase-space metric becomes $\tilde{M}=TMT^\dagger$. In more detail, one can write

$$\tilde{M}=\begin{bmatrix}ic^*Cc^T & 0 & ic^*Cr^T & ic^*Cp^T\\ 0 & -icC^*c^\dagger & -icC^*r^\dagger & -icC^*p^\dagger\\ ir^*Cc^T & -irC^*c^\dagger & ir^*Cr^T-irC^*r^\dagger & -I+ir^*Cp^T-irC^*p^\dagger\\ ip^*Cc^T & -ipC^*c^\dagger & I+ip^*Cr^T-ipC^*r^\dagger & ip^*Cp^T-ipC^*p^\dagger\end{bmatrix}. \tag{3.35}$$

The dynamical equations in the new coordinates are then given by

$$\begin{bmatrix}iC & 0 & iC_R & iC_P\\ 0 & -iC^* & -iC_R^* & -iC_P^*\\ iC_R^\dagger & -iC_R^T & C_{RR} & -I+C_{RP}\\ iC_P^\dagger & -iC_P^T & I+C_{PR} & C_{PP}\end{bmatrix}\begin{bmatrix}\dot{\tilde{z}}\\ \dot{\tilde{z}}^*\\ \dot{R}\\ \dot{P}\end{bmatrix}=\begin{bmatrix}\partial E/\partial\tilde{z}^*\\ \partial E/\partial\tilde{z}\\ \partial E/\partial R\\ \partial E/\partial P\end{bmatrix}. \tag{3.36}$$

The matrices

$$(C_X)_{ph,ik}=\left.\frac{\partial^2\ln S(\tilde{z}^*,R',P',\tilde{z},R,P)}{\partial\tilde{z}^*_{ph}\partial X_{ik}}\right|_{R'=R,P'=P} \tag{3.37}$$

and

$$(C_{XY})_{ik,jl}=-2\,\mathrm{Im}\left.\frac{\partial^2\ln S(\tilde{z}^*,R',P',\tilde{z},R,P)}{\partial X'_{ik}\partial Y_{jl}}\right|_{R'=R,P'=P} \tag{3.38}$$

are defined with X and Y denoting R or P. The evolution equation for the overall phase becomes

$$\dot{\gamma}=-\mathrm{Im}\left[\mathrm{Tr}\left[\dot{z}\frac{\partial\ln S(\tilde{z}^*,R',P',\tilde{z},R,P)}{\partial\tilde{z}}\right]+\sum_l(\dot{\mathbf{R}}_l\cdot\nabla^{|\rangle}_{\mathbf{R}_l}\ln S+\dot{\mathbf{P}}_l\cdot\nabla^{|\rangle}_{\mathbf{P}_l}\ln S)\right]+\frac{1}{2}\sum_k(\mathbf{P}_k\cdot\dot{\mathbf{R}}_k-\dot{\mathbf{P}}_k\cdot\mathbf{R}_k)-E(\tilde{z}^*,\tilde{z},R,P)\ . \tag{3.39}$$

For simplicity, the tilde will be suppressed from now on, since the identity of the parameters used, with fixed or traveling atomic orbitals, will always be clear from the context.

3. Representation in an orthonormal basis built with traveling atomic orbitals

Because the terms C_R and C_P, Eq. (A14), and the energy derivative equation (A29) contain the factors of the metric C from Eq. (3.21), the dynamical equations (3.36) can again be simplified, i.e.,

$$i\dot{z}+i\sum_l(-z\quad I^{\circ})(\dot{\mathbf{R}}_l\cdot\nabla^{|\rangle}_{\mathbf{R}_l}\Delta+\dot{\mathbf{P}}_l\cdot\nabla^{|\rangle}_{\mathbf{P}_l}\Delta)\begin{bmatrix}I^{\bullet}\\ z\end{bmatrix}=(-z\quad I^{\circ})F\begin{bmatrix}I^{\bullet}\\ z\end{bmatrix}. \tag{3.40}$$

The nuclear part of Eq. (3.36) yields, with Eqs. (A14), (A15), (A30), and (A31),

$$\begin{aligned}\dot{\mathbf{P}}_k-\sum_l(C_{\mathbf{R}_k\mathbf{R}_l}\dot{\mathbf{R}}_l+C_{\mathbf{R}_k\mathbf{P}_l}\dot{\mathbf{P}}_l)+2\,\mathrm{Im}\,\mathrm{Tr}(C^{\dagger}_{\mathbf{R}_k}\dot{z})&=-\nabla_{\mathbf{R}_k}E\\ &=\sum_{l\neq k}\frac{Z_kZ_le^2(\mathbf{R}_k-\mathbf{R}_l)}{|\mathbf{R}_k-\mathbf{R}_l|^3}-\mathrm{Tr}(\nabla_{\mathbf{R}_k}h\Gamma)-\mathrm{Tr}[\mathrm{Tr}(\tfrac{1}{2}\nabla_{\mathbf{R}_k}V_{ab;ab}\Gamma)_a\Gamma]_b\end{aligned} \tag{3.41}$$

and

$$\begin{aligned}\dot{\mathbf{R}}_k+\sum_l(-C_{\mathbf{P}_k\mathbf{R}_l}\dot{\mathbf{R}}_l+C_{\mathbf{P}_k\mathbf{P}_l}\dot{\mathbf{P}}_l)-2\,\mathrm{Im}\,\mathrm{Tr}(C^{\dagger}_{\mathbf{P}_k}\dot{z})&=\nabla_{\mathbf{P}_k}E\\ &=\frac{\mathbf{P}_k}{M_k}+\mathrm{Tr}(\nabla_{\mathbf{P}_k}h\Gamma)+\mathrm{Tr}[\mathrm{Tr}(\tfrac{1}{2}\nabla_{\mathbf{P}_k}V_{ab;ab}\Gamma)_a\Gamma]_b\ .\end{aligned} \tag{3.42}$$

The total phase of the coherent state satisfies (3.39), which becomes

$$\begin{aligned}\dot{\gamma}=-\mathrm{Im}\,\mathrm{Tr}&\left[\dot{z}(I^{\bullet}+z^{\dagger}z)^{-1}z^{\dagger}+\sum_l(\dot{\mathbf{R}}_l\cdot\nabla^{|\rangle}_{\mathbf{R}_t}\Delta+\dot{\mathbf{P}}_l\cdot\nabla^{|\rangle}_{\mathbf{P}_l}\Delta)\Gamma\right]\\ &+\frac{1}{2}\sum_k(\mathbf{P}_k\cdot\dot{\mathbf{R}}_k-\dot{\mathbf{P}}_k\cdot\mathbf{R}_k)-E(z^*,z,R,P)\end{aligned} \tag{3.43}$$

for the determinantal state using Eqs. (A1) and (A6).

Approximating by neglecting the diatomic differential overlap effectively makes the atomic Slater-type-orbital basis orthogonal; so Eqs. (3.40)–(3.43) are valid for dynamics with semiempirical Hamiltonians that employ Slater-type orbitals. A brief definition of this approximation is given in Sec. 3 of the Appendix.

Field has implemented this form of the time-dependent Hartree-Fock equations with semiempirical Hamiltonians in his program DYNAMO (Field, 1992). However, he omits the C_R and C_{RR} terms.

Researchers using perturbed-stationary-states, close-coupling, and time-dependent Hartree-Fock methods for atom-atom collision have known for some time that the nonadiabatic coupling terms are very important and that their neglect can result in serious errors.

The C_R and C_{RR} terms coupling electrons and nuclei are also neglected in various formulations of dynamics on a computed surface, whether computed with conventional self-consistent fields (Carmer *et al.*, 1993; Zhao *et al.*, 1993) or with Car-Parrinello's simultaneous dynamics (Hartke and Carter, 1992). One could argue that in these methods there is an artificial decoupling of the electronic and nuclear motions during the dynamics. This has the consequence that the wave function does not move away from the Born-Oppenheimer surface. Including the nonadiabatic coupling terms addresses this problem properly, which is important for dynamical processes such as electron transfer (Newton, 1980, 1991; Larsson, 1981; Deumens *et al.*, 1987) and nuclear tunneling.

B. Nonorthogonal representation

In this section a second symplectic transformation that allows the description of the electronic state in terms of atomic orbitals is discussed. As previously stated, the theoretical derivations are transparent in an orthonormal basis. For the numerical calculations with *ab initio* Hamiltonians, it is advantageous, however, to be able to work in the atomic basis directly so that costly transformations to an orthonormal reference basis are avoided. An explicitly constructed coordinate transformation keeps the structure of the phase space and allows us to express the electronic state in terms of nonorthogonal atomic spin-orbitals. The dynamics is the same, but expressed in a different phase-space coordinate system. This is the framework used by the close-coupling, time-dependent Hartree-Fock (TDHF), and electron-nuclear dynamics (END) methods.

1. Symplectic transformation to raw atomic orbitals

The same notations as before are used for various quantities. For instance, the one- and two-electron integrals in the atomic basis are denoted as in an orthonormal basis. When confusion is possible, a tilde (~) is put over the symbol of the transformed quantity, just as in Sec. III.A.2. The *ab initio* Hamiltonian looks the same as in Eq. (3.1) except that the creators/annihilators are now associated with the atomic basis. The transformation between atomic and molecular bases for matrices, for example, the one- and two-electron integrals, is

$$h=W^{\dagger}\tilde{h}W \tag{3.44}$$

and

$$V=((W^{\dagger}((W^{\dagger}\tilde{V}_{ab;cd})_aW)_b)_cW)_d\ , \tag{3.45}$$

where the notation of this four-index transformation is using the contraction of a two-index matrix and a four-index matrix twice, such that $\{(WV_{ab;cd})_a\}_{xb;cd}=\sum_a W_{xa}V_{ab;cd}$. The transformed expressions refer only to quantities defined in the atomic basis. The computationally demanding step of explicitly transforming to an orthonormal molecular basis is then avoided. This is important for *ab initio* methods, but not relevant for the semiempirical approaches considered.

An appropriate set of parameters must be found so that the dynamic orbitals can be expressed directly in terms of the atomic basis. The parameters should be such that all important quantities (overlap, one-density, energy, metric, forces, etc.) can be expressed with only (pieces of) the atomic basis overlap matrix Δ (2.5) occurring and not the transformation matrix (2.19). The orbitals of the determinantal state are expressed in the atomic basis as

$$(\psi^{\bullet}\ \ \psi^{\circ})\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}=(\phi^{\bullet}\ \ \phi^{\circ})\begin{bmatrix} W^{\bullet} & W^{>} \\ W^{\vee} & W^{\circ} \end{bmatrix}\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}$$
$$=(\phi^{\bullet}\ \ \phi^{\circ})\begin{bmatrix} W^{\bullet}+W^{>}z \\ W^{\vee}+W^{\circ}z \end{bmatrix}. \tag{3.46}$$

Since the reference molecular basis is arbitrary except for its orthonormality, one is free to choose it with the aim of simplifying the expression of the dynamic molecular orbitals in the atomic basis. The principal goal is to maintain the same form of parametrization and keep all the properties found useful in terms of an orthonormal basis. It turns out that this can be accomplished. The details can be found in Sec. 2.a of the Appendix. Because the transformation preserves the form of the dynamical equations and the structure of the phase space, it is a symplectic transformation. In the next section the resulting dynamical equations are presented. Again, the tilde is omitted from the quantities to avoid complicated notation.

2. Representation in the nonorthogonal basis of traveling atomic orbitals

Starting with the metric Eq. (2.58) using Eq. (A66) with definitions for $\Lambda^{\bullet}$ Eq. (A57) and Λ° Eq. (A58), one can write

$$C_{ph,qg}=[(\Delta^{>\dagger}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(v\Delta^{>}+\Delta^{\circ})]_{pq}[\Lambda^{\bullet}(z)^{-1}]_{gh}\ . \tag{3.47}$$

The dynamical equations (3.36) become, with Eqs. (A67) and (A85),

$$(\Delta^{>\dagger}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(v\ \ I^{\circ})\left\{i\Delta\begin{bmatrix} 0 \\ \dot z \end{bmatrix}+\left[i\sum_l(\dot{\mathbf{R}}_l\cdot\nabla^{|\rangle}_{\mathbf{R}_l}\Delta+\dot{\mathbf{P}}_l\cdot\nabla^{|\rangle}_{\mathbf{P}_l}\Delta)-F\right]\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\right\}\Lambda^{\bullet}(z)^{-1}=0\ , \tag{3.48}$$

where the ket gradients of the overlap matrix $\Delta(R',P',R,P)$ act on the unprimed coordinates only. Because Δ is the overlap matrix of a basis, its rank is maximal and so is that of the leftmost matrix. The Λ matrices are invertible, and thus Eq. (3.48) can be satisfied if and only if

$$i(v\ \ I^{\circ})\Delta\begin{bmatrix} 0 \\ \dot z \end{bmatrix}+i\sum_l(v\ \ I^{\circ})(\dot{\mathbf{R}}_l\cdot\nabla^{|\rangle}_{\mathbf{R}_l}\Delta+\dot{\mathbf{P}}_l\cdot\nabla^{|\rangle}_{\mathbf{P}_l}\Delta)\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}=(v\ \ I^{\circ})F\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\ . \tag{3.49}$$

For the nuclear coordinates, it follows, with Eqs. (A67), (A68), (A86), and (A87), that

$$\begin{aligned}\dot{\mathbf{P}}_k-\sum_l(C_{\mathbf{R}_k\mathbf{R}_l}\dot{\mathbf{R}}_l+C_{\mathbf{R}_k\mathbf{P}_l}\dot{\mathbf{P}}_l)+2\,\mathrm{Im}\,\mathrm{Tr}(C^{\dagger}_{\mathbf{R}_k}\dot z)&=-\nabla_{\mathbf{R}_k}E\\ &=\sum_{l\neq k}\frac{Z_kZ_le^2(\mathbf{R}_k-\mathbf{R}_l)}{|\mathbf{R}_k-\mathbf{R}_l|^3}-\mathrm{Tr}(\nabla_{\mathbf{R}_k}h\Gamma-\nabla_{\mathbf{R}_k}\Delta\Gamma h\Gamma)\\ &\quad-\mathrm{Tr}[\mathrm{Tr}(\tfrac{1}{2}\nabla_{\mathbf{R}_k}V_{ab;ab}\Gamma-\nabla_{\mathbf{R}_k}\Delta\Gamma V_{ab;ab}\Gamma)_a\Gamma]_b\end{aligned} \tag{3.50}$$

and

$$\begin{aligned}\dot{\mathbf{R}}_k+\sum_l(-C_{\mathbf{P}_k\mathbf{R}_l}\dot{\mathbf{R}}_l+C_{\mathbf{P}_k\mathbf{P}_l}\dot{\mathbf{P}}_l)-2\,\mathrm{Im}\,\mathrm{Tr}(C^{\dagger}_{\mathbf{P}_k}\dot z)&=\nabla_{\mathbf{P}_k}E\\ &=\frac{\mathbf{P}_k}{M_k}+\mathrm{Tr}(\nabla_{\mathbf{P}_k}h\Gamma-\nabla_{\mathbf{P}_k}\Delta\Gamma h\Gamma)\\ &\quad+\mathrm{Tr}[\mathrm{Tr}(\tfrac{1}{2}\nabla_{\mathbf{P}_k}V_{ab;ab}\Gamma-\nabla_{\mathbf{P}_k}\Delta\Gamma V_{ab;ab}\Gamma)_a\Gamma]_b\ .\end{aligned} \tag{3.51}$$

Note that at $R'=R$, the equality $\Delta^{\vee\dagger}=\Delta^{>}$ holds. The global phase of the molecular state satisfies Eq. (3.39), which with Eq. (A62) becomes

$$\dot{\gamma}=-\operatorname{Im}\operatorname{Tr}\left[\dot{z}\Lambda^{\bullet}(z)^{-1}(\Delta^{>}+z^{\dagger}\Delta^{\circ})+\sum_{l}(\dot{\mathbf{R}}_l\cdot\nabla_{\mathbf{R}_l}^{|\rangle}\Delta+\dot{\mathbf{P}}_l\cdot\nabla_{P_l}^{|\rangle}\Delta)\Gamma\right]+\frac{1}{2}\sum_{k}(\mathbf{P}_k\dot{\mathbf{R}}_k-\dot{\mathbf{P}}_k\mathbf{R}_k)-E(z^*,z,R,P)\ . \tag{3.52}$$

This equation can be integrated along with the dynamical equations (3.49)–(3.51).

The above dynamical equations have been implemented in the program ENDyne (Deumens, Diz, and Taylor, 1992) for general molecular systems and *ab initio* Hamiltonians (Deumens, Diz, Taylor, and Öhrn, 1992; Diz, 1992; Öhrn *et al.*, 1992; Longo, 1993).

C. Analysis

In this section different aspects of the equations for electron-nuclear dynamics obtained in the previous section are analyzed. Comparisons are made with the equations derived and implemented in various time-dependent approaches.

1. Molecules in inertial motion

Integration of Eqs. (3.40)–(3.42) or (3.49)–(3.51) with the proper initial conditions determines the evolution of the system. Proper initial conditions consist of positions and momenta of all nuclei involved and a set of electronic parameters. To describe an atomic or molecular collision or a process of intramolecular charge transfer at this level of theory, one would select an initial state that can be approximated by a single determinant. When a more complicated initial state is needed, for example, a multiconfigurational state (Deumens *et al.*, 1991), the electronic wave function has to be generalized from what is assumed here; but the procedure remains essentially the same.

The best single determinant for a given nuclear geometry can be obtained via an ordinary electronic structure self-consistent-field (SCF) calculation. However, when the initial nuclear momenta are not zero, the static electronic structure result is not a correct initial condition; molecular-dynamics theories sometimes use ETF's to address this problem. Another way is to consider the nonstatic equations for electronic states, which include the effect of the velocity of the nuclei in uniform motion.

a. Using traveling atomic orbitals

For a molecular system moving rigidly with velocity $\mathbf{V}$ and without acceleration, it is obvious that the parameters describing the electronic structure with respect to orbitals moving with the molecular frame stay unchanged. This is a result of the Galilei covariance of the Schrödinger equation, which is retained in the approximate dynamical equations. To express that an electronic state is a SCF solution moving with the molecule, one puts $\dot{z}=0$ in Eq. (3.40) to find

$$(-z\quad I^{\circ})\left[F-i\mathbf{V}\cdot\sum_{l}\nabla_{\mathbf{R}_l}^{|\rangle}\Delta\right]\begin{bmatrix}I^{\bullet}\\ z\end{bmatrix}=0 \tag{3.53}$$

as the equation for the electronic structure of a molecule in uniform motion. Here the Fock matrix is defined by Eq. (3.23).

b. Using orbitals fixed in space

The static electronic SCF solution in terms of orbitals fixed in space is the state that, for a given geometry, does not change in time,

$$i\dot{z}=0=(-z\quad I^{\circ})F\begin{bmatrix}I^{\bullet}\\ z\end{bmatrix}\ . \tag{3.54}$$

This defines a set of parameters z for each geometry $z=z_{\mathrm{HF}}(R)$. The change in $z_{\mathrm{HF}}(R)$ which is solely due to changes in geometry δR can be obtained by solving

$$\begin{aligned}0=&(-\nabla_{\mathbf{R}_k}z_{\mathrm{HF}}\quad 0)F\begin{bmatrix}I^{\bullet}\\ z_{\mathrm{HF}}\end{bmatrix}+(-z_{\mathrm{HF}}\quad I^{\circ})F\begin{bmatrix}0\\ \nabla_{\mathbf{R}_k}z_{\mathrm{HF}}\end{bmatrix}\\ &+(-z_{\mathrm{HF}}\quad I^{\circ})\nabla_{\mathbf{R}_k}F\begin{bmatrix}I^{\bullet}\\ z_{\mathrm{HF}}\end{bmatrix}\end{aligned} \tag{3.55}$$

for each nuclear coordinate $\mathbf{R}_k$. These are the coupled perturbed Hartree-Fock (Dalgaard and Jørgensen, 1978) equations used in electronic structure theory to derive the effect of external fields and geometry changes on SCF solutions. Similar equations hold for the dependence on nuclear momenta; but since the Fock operator does not depend on the nuclear momenta, the effect is zero.

When an atom or molecule is rigidly moving in space with uniform velocity $\mathbf{V}$, the corresponding change in z should reflect that the electronic state is following the nuclei with the same velocity but is otherwise unchanged; i.e.,

$$\begin{aligned}z(t+\delta t)&=z(t)+\dot{z}(t)\delta t\\ &=z_{\mathrm{HF}}(R(t))+\sum_{k}\nabla_{\mathbf{R}_k}z_{\mathrm{HF}}(R(t))\cdot\mathbf{V}\delta t\end{aligned} \tag{3.56}$$

and hence

$$\dot{z}(t)=\sum_{k}\nabla_{\mathbf{R}_k}z_{\mathrm{HF}}(R(t))\cdot\mathbf{V}\equiv w\ . \tag{3.57}$$

The correct dynamic electronic state is therefore given by solving the coupled system

$$
\begin{aligned}
iw &= (-z \quad I^{\circ})F\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix} , \\
0 &= (-w \quad 0)F\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix} + (-z \quad I^{\circ})F\begin{bmatrix} 0 \\ w \end{bmatrix} \\
&\quad + (-z \quad I^{\circ})\sum_k \nabla_{\mathbf{R}_k} F\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix} \cdot \mathbf{V}
\end{aligned}
\tag{3.58}
$$

for the matrices z and w. This is equivalent to solving Eq. (3.53).

In the representation using nonfollowing orbitals, the basis has to be good enough to describe translation (solving for w), whereas the description in the representation with traveling AO's is manifestly Galilei covariant. The generalization of this equation to the representation in the atomic basis is obvious. The solution of Eq. (3.53) or (3.58) allows one to set up the proper initial conditions for most atomic and molecular collision processes.

2. Linearized equations

The linear approximation to the system of equations derived from the TDVP can be obtained and yields the generalizations for moving nuclei of the well-known random-phase approximation or, equivalently, the coupled Hartree-Fock equations. The random-phase approximation (RPA) is, in fact, sometimes referred to as "linearized TDHF." The z parameters can be identified as RPA amplitudes, thereby clarifying their physical meaning. The form of the solution gives valuable insight as to how the z parameters evolve in time. The evolution of an electronic state involves many high-frequency modes. Because of their high frequency, they impose small time steps in the differential equation solver. In this way a lot of effort is spent to accomplish something which is not really that informative. Ideally, one would want to integrate the system with time steps characteristic of the nuclear dynamics. Micha and collaborators (Runge *et al.*, 1990; Feng *et al.*, 1991; Micha and Runge, 1992) linearize the electronic part of the equations and solve that part analytically. This leaves the nuclear motion for the numerical integration, which then progresses with time steps determined by changes in the electronic density, which are of the same order as the nuclear time steps except when a transition occurs. When that is the case, one is, of course, interested in the details of the process, whatever its time scale. Theilhaber (1992) uses a procedure borrowed from simulations of plasma oscillations, which involves scaled-down masses for the nuclei during the evolution and extrapolation of the results to relevant time scales.

It is instructive to rewrite the dynamical equation for the electrons explicitly in terms of the Thouless parameters z as a linear array ζ. For example, in the space-fixed basis, Eq. (3.22) looks very simple as it is written in terms of the rectangular matrix z. However, it is a highly nonlinear equation, which can be shown most clearly when it is written in terms of the Thouless coefficients arranged as a linear array ζ as defined in Eq. (2.45). The explicit derivation, since it is tedious but straightforward, will not be given here. It suffices to sketch the reasoning. Each term is a multilinear function in ζ and ζ^* of order (n,m), i.e.,

$$
C^{(n,m)}\underbrace{\zeta^*\ldots\zeta^*}_{n}\,\underbrace{\zeta\ldots\zeta}_{m} . \tag{3.59}
$$

The multilinear coefficients C always contain the normalization factor

$$
N(\zeta^*,\zeta) = [I^{\bullet} + L^{T}(\zeta^*)L(\zeta)]^{-1} , \tag{3.60}
$$

where $z_{ph} = L(\zeta_\alpha)_{ph}$ is the mapping from the linear array ζ to the rectangular z. Using this information, we can write Eq. (3.22) as

$$
\begin{aligned}
i\dot{\zeta} &= f(\zeta^*,\zeta) + A(\zeta^*,\zeta)\zeta + B(\zeta^*,\zeta)\zeta^* \\
&\quad + C^{(0,2)}(\zeta^*,\zeta)\zeta\zeta + C^{(1,1)}(\zeta^*,\zeta)\zeta^*\zeta \\
&\quad + C^{(0,3)}(\zeta^*,\zeta)\zeta\zeta\zeta + C^{(1,2)}(\zeta^*,\zeta)\zeta^*\zeta\zeta \\
&\quad + C^{(1,3)}(\zeta^*,\zeta)\zeta^*\zeta\zeta\zeta .
\end{aligned}
\tag{3.61}
$$

These are the nonlinear TDHF equations. They have up to fourth-order multilinear terms which include a normalization factor that is the inverse of a bilinear term in the coefficients. The equation can be written with any state $|\zeta_0\rangle$ as the reference leading to factors ζ-ζ_0 instead of ζ in Eq. (3.61).

The linearized TDHF are obtained by omitting all but the first three terms on the right-hand side, and by setting the normalization factor equal to the unit matrix. The explicit expressions for the coefficients follow from the derivation, but are not useful for practical computation of the linear equations. It is much simpler to obtain the coefficients from a Taylor expansion of the energy. The first (gradient) and second derivative (Hessian) of the energy and of the logarithm of the overlap of the determinantal state are needed with respect to the parameters ζ and the nuclear coordinates R and P at a given state ζ_0, R_0, P_0 around which the linear approximation is constructed. The vectors (gradients)

$$
f = \frac{\partial E}{\partial \zeta^*}, \quad m = \frac{\partial E}{\partial R}, \quad n = \frac{\partial E}{\partial P} , \tag{3.62}
$$

and matrices (Hessians)

$$
\begin{aligned}
A &= \frac{\partial^2 E}{\partial \zeta^* \partial \zeta}, \quad B = \frac{\partial^2 E}{\partial \zeta^* \partial \zeta^*} , \\
F &= \frac{\partial^2 E}{\partial \zeta^* \partial R}, \quad G = \frac{\partial^2 E}{\partial \zeta^* \partial P} , \\
I &= \frac{\partial^2 E}{\partial R \partial R}, \quad J = \frac{\partial^2 E}{\partial P \partial P}, \quad K = \frac{\partial^2 E}{\partial R \partial P}
\end{aligned}
\tag{3.63}
$$

are the necessary quantities. The gradient vectors and the Hessian matrices are given in Sec. 1.c of the Appendix for an orthonormal basis, Eqs. (A29)–(A31) and (A32)–(A37), and in Sec. 2.e for the atomic basis, Eqs. (A85)–(A87), (A32) and (A33), and (A88) and (A89).

With these definitions the equations, (3.36) or (3.61), have the linearized form

$$\begin{aligned} -iC\dot{\zeta} &= f + A(\zeta-\zeta_0)+B(\zeta^*-\zeta_0^*) \\ iC^*\dot{\zeta}^* &= f^* + B^*(\zeta-\zeta_0)+A^*(\zeta^*-\zeta_0^*) \ , \end{aligned} \tag{3.64}$$

where A is Hermitian and B is symmetric. These are the well-known RPA equations, also known as Coupled Hartree-Fock and linearized TDHF equations. Sometimes they are simply called TDHF equations. It is now clear that the Thouless coefficients are the RPA amplitudes. These equations are studied in detail by Deumens and Öhrn (1989a), and the main points of the analysis are repeated below. Let the total number of coordinates be N. Defining the matrices

$$\begin{aligned} \mathbf{C} &= \begin{bmatrix} C & 0 \\ 0 & -C^* \end{bmatrix}, \quad \mathbf{A} = \begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix}, \\ \mathbf{z} &= \begin{bmatrix} \zeta \\ \zeta^* \end{bmatrix}, \quad \mathbf{f} = \begin{bmatrix} f \\ f^* \end{bmatrix}, \end{aligned} \tag{3.65}$$

we can write the dynamical equation (3.64) as

$$-i\mathbf{C}\dot{\mathbf{z}} = \mathbf{f} + \mathbf{A}(\mathbf{z}-\mathbf{z}_0) \ . \tag{3.66}$$

This first-order differential equation is solved by introducing new coordinates

$$\tilde{\mathbf{z}} = \begin{bmatrix} \tilde{\zeta} \\ \tilde{\zeta}^* \end{bmatrix}, \tag{3.67}$$

the *normal-mode amplitudes,* and a constant vector $\mathbf{g}$ to eliminate the inhomogeneous term,

$$\mathbf{z} = \mathbf{T}e^{i\Omega t}\tilde{\mathbf{z}} + \mathbf{g} \ , \tag{3.68}$$

or in block form

$$\begin{bmatrix} \zeta \\ \zeta^* \end{bmatrix} = \begin{bmatrix} X & Y \\ Y^* & X^* \end{bmatrix} \begin{bmatrix} e^{i\Omega t} & 0 \\ 0 & e^{-i\Omega t} \end{bmatrix} \begin{bmatrix} \tilde{\zeta} \\ \tilde{\zeta}^* \end{bmatrix} + \begin{bmatrix} g \\ g^* \end{bmatrix} . \tag{3.69}$$

The eigenvalues and eigenvectors of $\mathbf{C}^{-1}\mathbf{A}$ are the elements of the diagonal matrix Ω and the columns of $\mathbf{T}$, respectively. The vector $\mathbf{g}$ satisfies

$$\mathbf{A}\mathbf{g} = -\mathbf{f} + \mathbf{A}\mathbf{z}_0 \tag{3.70}$$

and is therefore given by

$$\mathbf{g} = \mathbf{z}_0 - \mathbf{A}^{-1}\mathbf{f} \ . \tag{3.71}$$

The eigenvectors satisfy the normalization condition

$$\mathbf{T}^\dagger\mathbf{C}\mathbf{T} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} ; \tag{3.72}$$

the solution to (3.66) therefore is

$$\begin{aligned} \mathbf{z}(t) &= e^{i\mathbf{T}\Omega\mathbf{T}^{-1}t}[\mathbf{z}(0)-\mathbf{g}]+\mathbf{g} \\ &= e^{i\mathbf{C}^{-1}\mathbf{A}t}[\mathbf{z}(0)-\mathbf{g}]+\mathbf{g} \\ &= e^{i\mathbf{C}^{-1}\mathbf{A}t}[\mathbf{z}(0)-\mathbf{z}_0+\mathbf{A}^{-1}\mathbf{f}]+\mathbf{z}_0-\mathbf{A}^{-1}\mathbf{f} \ . \end{aligned} \tag{3.73}$$

Note the generalization of the exponent $i\mathbf{C}^{-1}\mathbf{A}$ in comparison to the solution of a simple oscillator problem. This is the first approximation to the full, nonlinear evolution of the z's and clearly shows that they can be identified with the RPA amplitudes. When $B=0$ the Tamm-Dancoff approximation is obtained or, equivalently, the configuration interaction with single excitations (CIS). This corresponds to maintaining the reference state as the ground state and obtaining approximate eigenstates in terms of selected single orbital promotions out of that state. Including the B yields the RPA. It can be described as a perturbation-theory correction to CIS or to the Tamm-Dancoff approximation, where some effect of double excitations on the ground state is included.

The linearized solution can be used in two different ways. On the one hand, the locally linearized solution can be used as the zero-order term in an expansion, as done by Micha and co-workers (Runge *et al.*, 1990; Feng *et al.*, 1991); the fast modes in the zero-order term can be directly propagated during a long time step, providing a consistent procedure for the time step to grow and shrink during the evolution. This has been implemented by Runge (1993) under the assumption that the nonlinear corrections to the evolutions can be safely neglected. The results obtained by Runge, indeed, indicate that to be true for the cases studied.

On the other hand, the linearization can be used to define a symplectic transformation from the Thouless parameters ζ to the normal-mode amplitudes $\tilde{\zeta}$ [Eq. (3.68)]. This will transform the dynamical equations to an interaction picture where the main effect of the fast modes is explicitly eliminated without approximating the nonlinear equations. This transformation ensures that the main behavior of the new variables $\tilde{\zeta}$ will be slow, i.e., change at nuclear time scales. The high-frequency corrections to the slow motion will have small amplitudes if, as found by Runge, the linearized equations are a good approximation. The numerical integrator therefore proceeds with large time steps when integrating the new variables; and whenever the equations require smaller time steps, it will automatically adjust. Implementing the symplectic transformation, again with coordinate charts in the spirit of differential geometry, results in an efficient algorithm with the advantages of the methods that linearize the fast modes, but without any approximation. One keeps using the same chart, i.e., the same normal modes, until the equations show the deviations to be too large. Then new normal modes are constructed and a new chart is entered.

3. Equation for the density

The evolution equation for the density matrix deserves consideration. Let us use the notation

$$M = (I^{\bullet} + z^\dagger z)^{-1} \ . \tag{3.74}$$

Then the expression for the one-density, Eq. (A21), yields

$$i\frac{d}{dt}\begin{bmatrix} I^\bullet \\ z \end{bmatrix} M(I^\bullet \;\; z^\dagger)=\begin{bmatrix} 0 \\ i\dot{z} \end{bmatrix} M(I^\bullet \;\; z^\dagger)+\begin{bmatrix} I^\bullet \\ z \end{bmatrix} M(0 \;\; i\dot{z}^\dagger)-\begin{bmatrix} I^\bullet \\ z \end{bmatrix} M(0 \;\; i\dot{z}^\dagger)\Gamma-\Gamma\begin{bmatrix} 0 \\ i\dot{z} \end{bmatrix} M(I^\bullet \;\; z^\dagger)$$
$$=(I-\Gamma)\begin{bmatrix} 0 & 0 \\ -z & I^\circ \end{bmatrix} F\Gamma-\Gamma F\begin{bmatrix} 0 & -z^\dagger \\ 0 & I^\circ \end{bmatrix}(I-\Gamma) , \tag{3.75}$$

where Eq. (A10) for the derivative of the inverse of a matrix is used. With the application of Eq. (2.28), Eq. (1.7) yields

$$\begin{aligned} i\dot{\Gamma}&=(I-\Gamma)F\Gamma-\Gamma F(I-\Gamma) \\ &=F\Gamma-\Gamma F . \end{aligned} \tag{3.76}$$

The linearization in the time evolution defined by Runge and Micha is compared below with the usual linearized TDHF or RPA or Coupled Hartree-Fock. They use the Fock matrix F_0 at the reference state to propagate the density for a time step according to

$$\dot{\rho}=F_0\rho-\rho F_0 . \tag{3.77}$$

In terms of the basis of eigenvectors of the Fock matrix with eigenvalue matrix ε_0, the solution is written as

$$\rho(t)=e^{i\varepsilon_0 t}\rho_0 e^{-i\varepsilon_0 t}=U^\dagger\rho_0 U . \tag{3.78}$$

Using the ground-state determinant at t_0 as the reference state and expressing it in the Thouless representation with Thouless parameters z_0 and with M as defined above, one can write

$$\begin{aligned} \rho(t)&=\begin{bmatrix} U^{\bullet\dagger}MU^\bullet & U^{\bullet\dagger}Mz_0^\dagger U^\circ \\ U^{\circ\dagger}z_0MU^\bullet & U^{\circ\dagger}z_0Mz_0^\dagger U^\circ \end{bmatrix} \\ &\approx\begin{bmatrix} I^\bullet & U^{\bullet\dagger}z_0^\dagger U^\circ \\ U^{\circ\dagger}z_0U^\bullet & 0 \end{bmatrix} , \end{aligned} \tag{3.79}$$

through terms linear in z_0. Therefore the zero-order linearization used by Runge and Micha is equivalent to a time evolution of the Thouless coefficients expressed as

$$z(t)=e^{i\varepsilon_0^\circ t}z_0e^{-i\varepsilon_0^\bullet t} , \tag{3.80}$$

which means for the matrix elements that

$$z_{ph}(t)=e^{i(\varepsilon_{0p}-\varepsilon_{0h})t}z_{0ph} . \tag{3.81}$$

The solution for the (first-order) linearized TDHF or RPA (Deumens and Öhrn, 1989a) is given by Eq. (3.73),

$$\begin{aligned} \mathbf{z}(t)&=\mathbf{T}e^{i\Omega t}\mathbf{T}^{-1}\mathbf{z}_0 , \\ \zeta(t)&=(Xe^{i\Omega t}X^\dagger-Ye^{-i\Omega t}Y^\dagger)C\zeta_0 \\ &\quad+(Xe^{i\Omega t}Y^T-Ye^{-i\Omega t}X^T)C^*\zeta_0^* , \end{aligned} \tag{3.82}$$

which for the simplest case of the Tamm-Dancoff approximation or CIS, where $Y=0$, becomes explicitly

$$z_{ph}(t)=\sum_{qg}\sum_{rf}\sum_{se}X_{ph,qg}e^{i\Omega_{qg}t}X^*_{qg,rf}C_{rf,se}z_{0se} . \tag{3.83}$$

This equation has a sum of terms with the Tamm-Dancoff approximation or CIS frequencies in the exponential factor, which is to be compared with a single term with the orbital energy differences in the exponential in Eq. (3.81).

4. Velocity-dependent terms

In this section the terms in the dynamical equations that depend on the velocity of the nuclei are discussed. These terms have been the subject of discussions (Delos, 1981) among the proponents of the close-coupling method and of the perturbed-stationary-state (PSS) method. The close-coupling method claims (Delos, 1981) to avoid an inconsistent treatment of terms linear in the velocity present in the original PSS treatment. However, the PSS method in its present form has overcome this shortcoming (Riera, 1992). Equations (3.40)–(3.42), or in the atomic basis, Eqs. (3.49)–(3.51), derived in this review can be viewed as a generalization of the perturbed-stationary-state equations to include fully dynamical trajectories when ordinary AO's are used and as a generalization of the close-coupling equations when traveling atomic orbitals (TAO's) are employed.

The terms dependent on the nuclear velocities show the same "inconsistency" as the PSS method does when ordinary atomic orbitals are used. Equation (3.40) includes the terms that are dependent on the nuclear velocities $\dot{\mathbf{R}}_l$, known as the nonadiabatic coupling terms and appearing in the close-coupling form of the equations as the term $\mathbf{P}$ in Eq. (1.18). But this equation has none of the other terms in Eq. (1.18).

When traveling atomic orbitals are used, the equations derived here include all terms. To be specific, we consider the Hamiltonian (3.1), which does not include any velocity-dependent terms such as spin-orbit coupling. Let us now compare the equations in a given basis of ordinary AO's ϕ with the equations obtained in the corresponding basis of traveling AO's $\beta\phi$, the correspondence being that the traveling AO's are constructed from the ordinary AO's by multiplication with the electron translation factor (ETF) β given by Eq. (2.16). The electronic kinetic-energy operator in the Fock operator part of Eq. (3.40) acting on an atomic orbital at center l gives three terms

$$\frac{1}{2}mV^2\beta\phi-i\beta\mathbf{V}\cdot\nabla_{\mathrm{r}}\phi-\frac{1}{2m}\beta\nabla_{\mathrm{r}}^2\phi \tag{3.84}$$

where atomic units are used, as before. The first term is a shift of the energy. The second term comes from the motion of the electron with the center, as described by the ETF, and is the important term. The third term is the kinetic energy of the ordinary AO. The nonadiabatic coupling term in Eq. (3.40) can be written as

$$i\dot{\mathbf{R}}_l\cdot\nabla_{\mathbf{R}_l}(\beta\phi)=-i\beta\mathbf{V}_l\cdot\nabla_{\mathbf{r}}\phi\ , \tag{3.85}$$

where the property used is that the orbitals only depend on the difference $\mathbf{r}-\mathbf{R}_l$, such that derivatives with respect to the electron coordinates are equal to the negative of the derivative with respect to the corresponding nuclear ones. This term gives the cancellation between the **P** and **A** terms in Eq. (1.18), which, as discussed by Delos (1981), makes the close-coupling method much less sensitive to basis-set size effects than the original formulation of the PSS method.

All matrix elements, to first order in velocity, yield extra terms between derivative basis functions, as can be seen most easily by expanding the ETF as in Eq. (2.17). Most close-coupling applications do not evaluate the matrix elements with the ETF, but approximate them by assuming the ETF to be constant over the volume of integration (Delos, 1981; Kimura and Lane, 1990; Fritsch and Lin, 1991). Several groups have developed and implemented algorithms to evaluate the multicenter integrals with Gaussian-type atomic-orbital basis sets (Errea *et al.*, 1979; Colle *et al.*, 1988), but their codes do not seem to be widely used.

The first PSS calculations used explicit molecular orbitals for diatomic systems, for which the derivatives with respect to one atomic center are not simple. Modern calculations tend to use linear combinations of atomic orbitals as molecular basis functions, and the AO's are usually chosen as a succession of *s*-, *p*-, and *d*-shell orbitals. As a result, the gradients in the nonadiabatic coupling terms *P* can be represented exactly in the basis, leaving only the highest shell without a converged representation of the derivatives, because derivatives, with respect to the center of orbitals in one shell, can be expressed as linear combinations in the same or the next shell. This is the reason why the modern PSS calculations do not suffer (Riera, 1992) from the imbalance introduced by considering only the nonadiabatic coupling term and leaving all other terms to the completeness of the basis. As a result, the differences between the close-coupling and PSS methods in this respect, which were sizable a decade ago (Delos, 1981), are not as important anymore (Riera, 1992).

The results discussed in Sec. IV, which are all obtained with ordinary AO's, i.e., without ETF's, illustrate what can be accomplished through the flexibility of using linear combinations of atomic orbitals as the basis. In those applications the basis achieves all that TAO's can, and only at high energies is the need for inclusion of ETF's necessary, either explicitly, as in the close-coupling method,or implicitly, as in the PSS method.

5. Acceleration-dependent terms

Much of the attention given ETF's is centered on the properties of a basis set with such functions at the asymptotic limit. If basis functions with ETF's are used, then they not only depend on the nuclear position, but also on the nuclear velocity through the velocity of the nuclear center, e.g., v appearing in Eq. (2.16).

In an atomic or molecular collision, acceleration of the nuclei will excite the electrons. When straight-line trajectories with fixed nuclear velocities are used to approximate the nuclear motion in collisions, these excitations are ignored. However, if the full dynamics of the system is studied, or if curved (e.g., Coulomb) trajectories are used, then the excitation due to acceleration in the interaction region should be taken into account. These excitations are accounted for by the terms coupling nuclear accelerations to the electronic coefficients seen in Eqs. (3.40)–(3.42) or (3.49)–(3.51).

With an ETF β as given by Eq. (2.16), the term $C_{\mathbf{P}}$ in the metric, which couples the nuclear accelerations to $\dot{z}$, has contractions over elements

$$\langle\beta'\phi'|\nabla_{\mathbf{P}_l}\beta\phi\rangle\propto\delta_{lk}\frac{m}{M_l}\langle\beta'\phi'|\mathbf{r}|\beta\phi\rangle \tag{3.86}$$

[see Eq. (A14)], where k is the nuclear center of orbital ϕ, and M_l is the mass of the nucleus at center l. These elements are proportional to dipole couplings. Since a derivative term with respect to $\mathbf{P}_l$ is multiplied by $\dot{\mathbf{P}}_l$, division by M_l has the effect of making the coupling proportional to the nuclear acceleration.

These couplings are of greater importance for head-on or near-head-on collisions, where greater accelerations are expected. They may be crucial for obtaining correct alignment and orientation properties of electrons in collisions at energies below 1 keV per atomic mass unit, where, for example, excitations to p states in a proton-hydrogen collision will be important only at small impact parameters. To the best of our knowledge, these couplings have not yet been taken into account.

IV. APPLICATIONS

A. Implementation

The END equations have been implemented in the computer code ENDyne[3] (Deumens, Diz, and Taylor, 1992), which is presently at version 2, release 4. The computational core of ENDyne consists of the routine that computes the gradient of the energy with respect to the Thouless parameters and the nuclear positions and momenta (forces), Eq. (A85), and the Hessian of the overlap

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[3] The program was originally called DYNAMO, but that name conflicts with the name of the program created by Field (1992).

matrix element (symplectic structure), Eq. (3.47). These gradients are used to solve the time-dependent equations for dynamics and for gradient-based optimization methods to find both ground and excited stationary states.

The TDVP produces an approximation to the time-dependent Schrödinger equation in the form of a system of coupled first-order ordinary differential equations [(3.49) and (3.50)]. Methods for solving such systems have been available for some time. Several methods exist, each with advantages and disadvantages. Because some methods work better in some situations than others, it is worthwhile to have the flexibility to use the one best suited to each problem. A good introduction can be found in *Numerical Recipes,* a classic by Press *et al.* (1986).

Solving a first-order differential equation numerically is basically very simple: one approximates the derivative with the difference formula and finds a value for the variable at the next time step. This is known as the Euler method. Its major disadvantage is that, in order to achieve high accuracy, very small time steps have to be taken. Three of the major methods are as quoted from *Numerical Recipes:*

(1) *Runge-Kutta* methods propagate a solution over an interval by combining the information from several Euler-style steps (each involving one evaluation of the right-hand-side of the equation) and then using the information obtained to match a Taylor series expansion up to some higher order.

(2) *Richardson extrapolation* uses the powerful idea of extrapolating a computed result to the value that *would* have been obtained if the stepsize had been much smaller than the one actually used. Extrapolation to zero stepsize is the goal. When combined with a particular way of taking individual steps (the *modified midpoint method*) and a particular kind of extrapolation (rational function approximation) Richardson extrapolation produces the Bulirsch-Stoer method.

(3) *Predictor corrector* methods store the solution along the way, and use these results to extrapolate the solution one step advanced. They then correct the extrapolation using derivative information at the new point. These are best for very smooth functions.

In the computer code three methods are implemented, which represent these categories:

(1) DE is a modified divided difference form of the Adams-Pece formulas and local extrapolation (Adams-Bashforth method). It adjusts the order and step size to control the local error. This method is fully explained in the text by Shampine and Gordon (1975).

(2) DRIVEB is a variant of the GEAR package (Hindmarsh, 1975). It also uses Adams methods or, optionally, backward differentiation formulas, otherwise known as the stiff methods of Gear. The package can use functional iteration (no partial derivatives needed), or the chord method with an analytic Jacobian supplied by the user or with the Jacobian constructed approximately by numerical differentiation.

(3) ODEINT uses Richardson extrapolation with the Bulirsch-Stoer method (Press *et al.*, 1986). This method is extremely accurate, but it requires many more points than any of the previous methods. Therefore it is used only to verify a part of the evolution, when one has reason to doubt the accuracy of the faster, simpler methods.

All the above methods adapt the step size to the scale of the solution, starting from a small guess and gradually increasing the step size if the estimated error indicates that the predicted solution is accurate.

The Adams-Bashforth method is usually fastest. Gear's method with backwards differentiation is necessary when the molecule has core orbitals that may acquire energy and start oscillating strongly because of numerical inaccuracies. The other methods will produce an unstable solution in that case. The Bulirsch-Stoer method is the most accurate, but requires the largest number of function evaluations, which are the most time-consuming part in an ENDyne simulation. It is recommended for benchmarking use only.

A conjugate gradient method (Fletcher-Reeves and Polak-Ribière) and a method with Hessian matrix (Davidon-Fletcher-Powell and Broyden-Fletcher-Goldfarb-Shanno) have also been implemented (Press *et al.*, 1986). These routines have been modified to use the basic linear algebra subroutines library for optimal vectorization. The algorithms have been generalized to work in curved spaces with non-Euclidean metric. This way they can properly work in the space of electronic variables and in the space of combined electronic and nuclear variables.

Either the optimization algorithm or a conventional SCF algorithm can be used to determine the initial electronic state for a given initial geometry (Deumens, Diz, Taylor, and Öhrn, 1992; Öhrn *et al.*, 1992; Longo, 1993). Initially ENDyne determines the optimal Thouless parametrization, one in which the z's are as small as possible. The code then proceeds to integrate the coupled differential equations with a user-selected algorithm, recording the history of the process in a file. This file is used for restarting the program if it crashes and for visualization of the dynamics. Several properties—such as total electronic momentum, total momentum, electron charge distribution as given by Mulliken population analysis, and eigenvalues of the projected Fock matrix—can also be computed, and these are written to the history file. ENDyne continuously monitors the size of the Thouless coefficients. If they become large compared to unity, it is assumed that the determinant wave function wants to move into a space orthogonal to the reference state. Then the program is forced to restart with a flag indicating that a new optimal reference state needs to be chosen. This means ENDyne is switching to a new coordinate chart. This procedure is completely automatic and very stable. ENDyne also uses this chart switch when the differential equation solver finds instabilities or sudden stiffness in the equations. This sometimes happens during the most violent part of a reaction. Experience shows that the switching of coordinate charts may happen only once or twice during a trajectory. For most trajectories, though, no chart switching is needed.

The implementation of the boosted SCF equations, Eq. (3.53), has been completed recently, as has the coding of the transformation, Eq. (3.68), to the interaction picture defined by the RPA. Other features include the use of a set of classical plane-wave electromagnetic pulses interacting with the electrons and nuclei through the long-wavelength approximation, and the inclusion of ETF's to first order in the nuclear velocity and for semiempirical Hamiltonians.

B. Ion-atom scattering

In this section some representative results obtained with the ENDyne code are analyzed and compared with experiment and other theoretical work.

1. Proton-hydrogen collisions

Proton-hydrogen collisions have been the subject of abundant experimental studies in the last 20 years. Thus they provide an excellent test for new time-dependent theoretical approaches to electron-nuclear dynamics.

Most theoretical work on this system is performed at collision energies above 1 keV in the lab frame. Calculations use either straight-line or Coulomb trajectories for the nuclei. Such approaches yield electron-transfer and excitation cross sections in agreement with experimental results, even if strict conservation laws of energy and total momentum are violated. However, for lower energies the motion of the proton is sufficiently slow that different trajectories significantly alter the results. It is then necessary to treat the electron-nuclear and nuclear-nuclear interactions correctly throughout the collision process and allow for fully dynamical trajectories.

Fritsch and Lin (1991), as well as Kimura and Lane (1990), recently published reviews on the semiclassical close-coupling method and examined proton-hydrogen collisions, as well as some other systems, in some detail. This method, and other methods they used as comparisons, use prescribed trajectories.

Fritsch and Lin employ the close-coupling scheme with an extended basis which they call the AO^+ method (Fritsch and Lin, 1982, 1983). It consists of a basis of 1*s*, 2*s*, 2*p*, and $n=3$ atomic orbitals corresponding to the free hydrogen atom, as well as atomic orbitals corresponding to the united atom (He). The He orbitals are expected to be important for small impact parameters. Their work explores the energy range 1–75 keV.

Runge, Micha, and Feng (1990) use the eikonal approximation to treat the nuclei and propagate the time-dependent electronic density matrix in the linearized TDHF approximation as described in Sec. I.B.4.d. They analyze proton-hydrogen collisions in the collisional energy range 10 eV–1 keV using only 1*s* states in the basis. They also investigate the effect of using straight-line trajectories, Coulomb trajectories, and effective potentials. They show the importance of using the correct trajectory for energies below 1 keV. More recently, calculations with larger basis sets have also been performed (Runge, 1993).

Few theoretical studies are done for energies below 1 keV. The most recent, by Hunter and Kuriyan (1977a, 1977b) for collision energies between 0.0001 eV and 10 eV, uses the time-independent perturbed-stationary-state (PSS) method to separate the nuclear degrees of freedom from the electronic ones. Davis and Thorson (1978) published a similar study, but for an energy range going from 0 to 0.2 eV and correcting for some errors in the work of Hunter and Kuriyan. The results for the two studies in the overlapping energy range are very similar. Comparisons with Hunter and Kuriyan's work are chosen, since the information they report is in the form of tables, while Davis and Thorson only publish low-precision graphs. In both these studies the nuclei are treated quantum mechanically, and only the molecular $1s\sigma$ and $2p\sigma$ states are used. Twenty years earlier, Dalgarno and Yadav (1953) also used the PSS approach to treat this problem for energies starting as low as 0.25 eV and going up to 100 keV. Even before that, Bates and Dalgarno (1952) studied this problem using the Born approximation, for the energy range 0–250 keV. Their results show that the Born approximation works well for energies above 10 keV, but fails for lower energies by several orders of magnitude.

The computer code ENDyne was used (Deumens, Diz, Taylor, and Öhrn, 1992) to calculate several properties of the proton-hydrogen collision as a first test of the general method. An energy range of 0.02–4000 eV is selected, which spans the very low energy regime investigated by Hunter and Kuriyan and by Davis and Thorson (Hunter and Kuriyan, 1977a, 1977b; Davis and Thorson, 1978), as well as some higher energies. Transfer or excitation probabilities to different orbitals are calculated by first projecting the results on a hydrogenic basis with an ETF. This can be done analytically with a Gaussian-type-orbital basis (Sec. II.A.2).

Approximate hydrogenic 1*s*, 2*s*, and 2*p* functions are expressed in terms of six Gaussians each. The 1*s* and 2*p* functions are taken from Stewart (1970). The 2*s* function was optimized to fit the hydrogenic 2*s* state. The coefficients and exponents used can be found in Table II.

Figure 1 plots the experimental total transfer cross sections and our calculations. The results reproduce experiments over five orders of magnitude in the kinetic energy of the colliding proton. Total cross sections of the scattering of H^+ on H are obtained by numerically integrating (Maitland *et al.*, 1981; Murrell and Bosanac, 1992)

$$\sigma(E)=2\pi\int_0^\infty bP(b;E)db \tag{4.1}$$

for several energies E, where b is the impact parameter and $P(b;E)$ the transfer probability as a function of b for

TABLE II. Contraction coefficients c and exponents α for the $2s$ function used in the $6G$ basis.

2s function[a]	
c	α
-3.75318×10^{-1}	1.21392×10^{-2}
-7.61767×10^{-1}	2.67784×10^{-2}
3.22382×10^{-2}	1.60950×10^{-1}
1.77665×10^{-1}	4.71398×10^{-1}
5.42463×10^{-2}	1.68965
1.01853×10^{-2}	9.22099

[a] Stewart (1970).

a given E obtained by projecting the evolved state on the appropriate final state (e.g., eigenstates of the moving proton for elastic processes, or various hydrogen-atom states for charge-transfer or excitation processes). The upper integration limit is chosen to be between 11.0 and 12.0 a.u. This choice is reasonable, since the transfer probability in this interval is smaller than 10^{-7}.

Excitation and transfer cross sections for $2s$ and $2p$ states, as well as integral alignment for the relative excitation of the various $2p$ target substates, have also been calculated, showing good agreement with experiment (Deumens, Diz, Taylor, and Öhrn, 1992).

Various basis sets have been tested, and in Table III contraction coefficients and exponents are given for an additional basis set used for proton on hydrogen, as well as a basis set used for the proton-helium studies. The polarized valence double zeta (pVDZ) basis set for H is the same as that of Dunning (1989), but with the s exponents scaled by $1.2^2=1.44$. The 6-31G* basis for He is not available in the literature, but is contained in the GAUSSIAN (Frisch *et al.*, 1988) and the GAMESS (Schmidt *et al.*, 1990) basis-set data banks. The contraction coefficients and exponents are listed in Table III.

Table IV summarizes the total-cross-section results obtained by the END method using two different sets of primitive functions in the basis sets.

As seen from Table IV, the basis set does not have a large effect in the calculated integral cross section for electron transfer in the H^++H collision. In addition, as noted in several of our earlier studies (Deumens, Diz, Taylor, and Öhrn, 1992; Diz, 1992; Longo, 1993), the END method with classical nuclei (and single-determinantal electronic wave function) provides excellent results for electron-transfer cross sections when compared with experimental data.

Since the integral cross section involves an integration, much of the detailed behavior of a charge-exchange collision is masked. Such details can be obtained from state-to-state cross section, differential cross section, and transfer probability as functions of the scattering angle and consequently provide a useful basis for theoretical model analysis. Below, results for the transfer probability and the reduced differential cross section as functions of the scattering angle are presented for the H^+ colliding with H at 250 eV. Results for a number of collision energies up to 2000 eV show similar agreement with experiments (Longo, 1993).

The equation for the differential cross section (σ_d) at a given collision energy E is (Maitland *et al.*, 1981; Murrell and Bosanac, 1992)

$$\sigma_d=\frac{d\sigma(\theta)}{d\Omega}=\frac{bP(b)}{\sin\theta|d\Theta/db|}\,, \tag{4.2}$$

where b, θ, $P(b)$, $\Theta\, d\Omega=\sin\theta\, d\theta\, d\phi$ are the impact parameter, the scattering angle, the transfer probability, the classical deflection function, and the solid angle, respectively. The modulus of $db/d\theta$ is used to ensure that the differential cross section is always a positive quantity. In addition, since the scattering angle by definition always lies between zero and π, it holds that $\sin\theta\geq 0$.

The experimental procedure (Helbig and Everhart, 1965; Houver *et al.*, 1974) consists of a mass-analyzed H^+ beam issued from a single discharge ion source

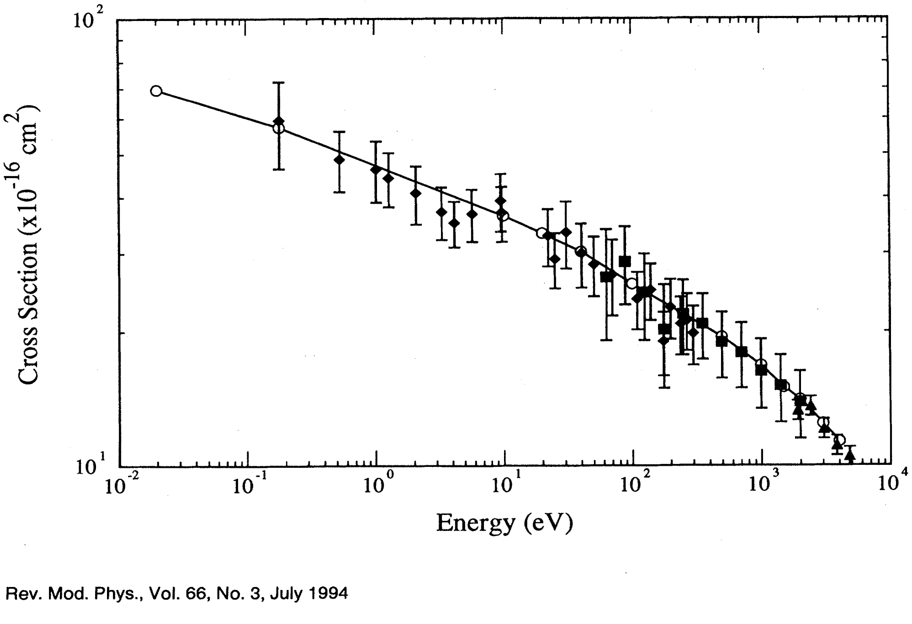

FIG. 1. Total transfer cross sections for H^++H at collision energies ranging from 0.02 eV to 4000 eV, in a comparison of experiment and END theory. The END results are the open circles joined by the solid line. Solid diamonds are from Newman *et al.* (1982); solid squares, Gealy and Zyl (1987); solid triangles, McClure (1966).

TABLE III. Contraction coefficients c and exponents α for the basis sets used in this work.

	$H/p\mathrm{VDZ}$[a]		He/6-31G^{*}[b]	
	c	α	c	α
1s function	0.01969	18.7344	0.02377	38.4216
	0.13798	2.82528	0.15468	5.77803
	0.47815	0.64022	0.46930	1.24177
2s function	0.50124	0.17568	0.29796	1.00000
2p function	1.00000	0.72700	1.10000	1.00000

[a] Dunning (1989).

[b] Frisch *et al.* (1988); Schmidt *et al.* (1990).

crossed with a thermal H beam. Ions and atoms scattered at a given angle are selected and analyzed. The overall energy resolution varies from 0.8 eV up to 2 eV in the 250 eV–2000 eV energy range. The uncertainties affecting the experimental results arise from (i) the finite angular resolution $\Delta\theta$ ($\pm 0.07^\circ$ for small angles, up to $\pm 0.2^\circ$ for large angles), (ii) the errors in the dissociation fraction determination (H/H_2 ratio in the collision region), and (iii) the accuracy of the relative calibrations of the cross sections for the different processes (elastic, charge transfer, and excitation). Because of the rapid variation of the transfer probability and the differential cross section with the angle, more particles arise from the region $\theta-\Delta\theta$ than from the region $\theta+\Delta\theta$. Thus the center angle is slightly larger than the one corresponding to the most probable scattering. However, this error never exceeds 0.1° (Helbig and Everhart, 1965; Houver *et al.*, 1974). As can be seen in the comparison between the experimental data and the END results, the finite angular resolution can account for most of the damping in the oscillatory behavior of the observed versus the calculated transfer probability and differential cross sections. Problems with the measured direction of the incident beam with respect to the detection system can be eliminated by studying the scattering on both sides of the incident-beam direction and choosing the zero index from the symmetry of the data curves. In addition to these uncertainties, the experimental results are normalized to theoretical results (Gaussorgues *et al.*, 1975) for the elastic differential cross section at small angles.

From the discussion of the experimental uncertainties it seems clear that the measured transfer probability versus the scattering angle is less susceptible to errors than is the differential cross section. It is also independent of scaling factors. Thus, in Fig. 2, results for the transfer probability are presented calculated by the ENDyne program and compared with experimental data. The theoretical procedure is the same as described in the calculation of the integral cross section. The only additional information needed is the asymptotic momentum of the proton, which is used to compute the scattering angle; that is,

$$\cos\theta=\frac{p_x}{p_{\mathrm{tot}}}=\frac{p_x}{\sqrt{p_x^2+p_y^2}}=\frac{1}{\sqrt{1+(p_y/p_x)^2}}\,, \tag{4.3}$$

where p_x and p_y are the x and y components of the asymptotic proton momentum.

Both the qualitative and quantitative features (position of maxima and minima) of the experimental data are very well reproduced by the END theory at the level of classical nuclei. The quantitative agreement can be made much better when an angular resolution window is applied to the theoretical data. This simulates the experimental resolution, results in a damping of the results, and explains why the oscillations in the transfer probability do not extend from zero to unity. It also should be mentioned that the semiclassical treatment (Gaussorgues *et al.*, 1975) using a three-term molecular basis provides results in perfect agreement with the experimental data. This is puzzling, since the experimental data have a damping of the oscillation due to the finite angular resolution, and the theoretical work does not mention how this damping is handled. Because of this the quantitative

TABLE IV. Total transfer cross section for H^+ colliding with a H ($\times 10^{-16}$ cm^2).

	Total transfer cross section		
Collision	END theory		
Energy (eV)	pVDZ basis	Hydrogen-6G basis	Experiment[a,b]
10	35.93	36.37	37.0±5.7
100	24.31	25.60	23.7±3.5
500	17.94	19.44	18.9±3.2
1000	16.55	16.78	16.3±2.9

[a] Newman *et al.* (1982).

[b] Gealy and Zyl (1987).

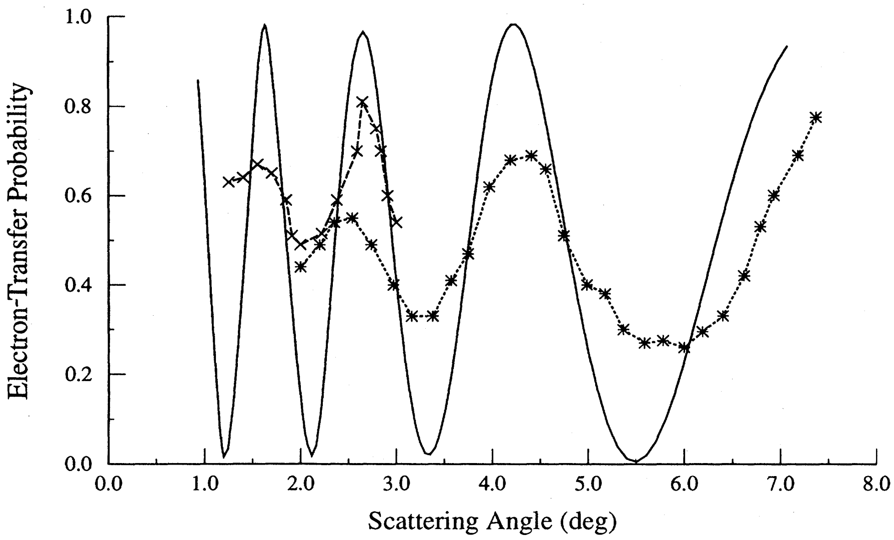

FIG. 2. Transfer probability vs the scattering angle (in degrees). The experimental and END results for the $H^+ + H$ system are compared. Energy: 250 eV. Basis set: *p*VDZ. Experimental angular resolution, ±0.6°; +, END; $*$, from Houver *et al.* (1974); ×, from Helbig and Everhart (1965).

agreement between the semiclassical method and the experimental results seems to be fortuitous, or the true meaning of the theoretical data is difficult to understand. Such damping is not observed in other theoretical treatments either (see, for example, Runge *et al.*, 1990).

The experimental results available for the $H^+ + H$ collision are often presented as "reduced" differential cross sections ρ, which are expressed as (Houver *et al.*, 1974)

$$\rho = \sigma_d \theta \sin\theta = \frac{b\theta P(b)}{|d\Theta/db|} . \tag{4.4}$$

This shows less rapid variation with the scattering than does the differential cross section. In Fig. 3 both elastic and charge-transfer reduced cross sections calculated using the ENDyne program at 250 eV are presented and compared with experimental data.

The same comments and conclusions about the transfer probability hold for the reduced differential cross section. One should only add that the agreement between the END numbers and experimental results for the reduced cross section is worse than for the transfer probability. The reduced differential cross section is explicitly dependent upon the scattering angle. The experimental data are normalized and fitted to some particular available theoretical results based upon prescribed trajectories. Thus one could argue that the experimental results for the reduced cross sections have been downgraded in quality by fitting to unsuitable theoretical results.

The importance of true dynamic trajectories at lower collision energies (below 1 keV) can be illustrated by the fact that differential cross sections involve derivatives of the deflection function. As an illustration the scattering angle as a function of impact parameter for proton–hydrogen-atom collisions at 500 eV obtained from fully dynamical END calculations is compared in Fig. 4 with those obtained with two different prescribed

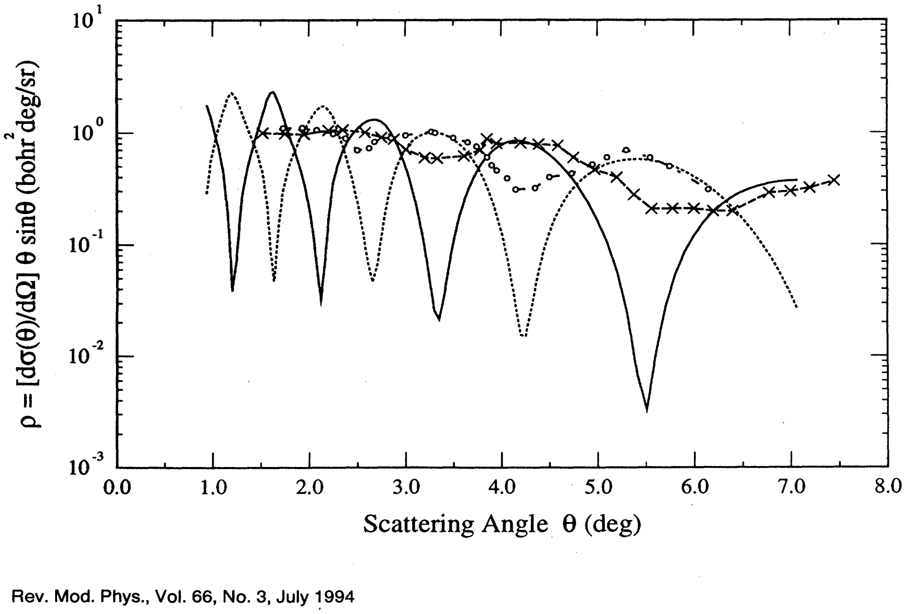

FIG. 3. Reduced differential cross sections vs the scattering angle. Experimental and END results for the $H^+ + H$ system are compared. Energy: 250 eV; basis set: *p*VDZ; $*$, END transfer; +, END elastic; and ×, transfer, and ○, elastic (from Houver *et al.*, 1974).

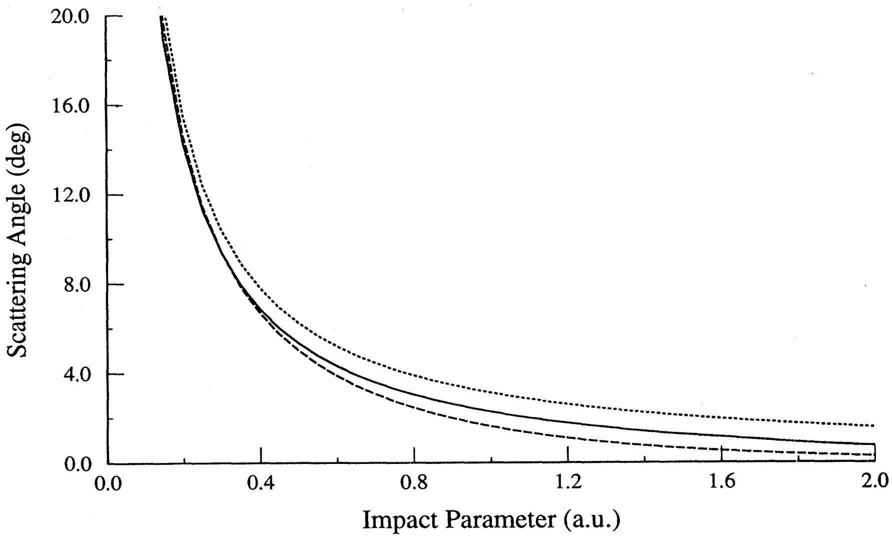

FIG. 4. Scattering angle as a function of impact parameter using END, bare nuclei, and hydrogen-atom potential for $H^+ + H$ system. There is a small impact-parameter region. Energy: 500 eV. Basis set: *p*VDZ. Scattering angle in degrees and impact parameter in a.u. Solid line, END; dotted line, bare nuclei; dashed line, hydrogen-atom potential.

trajectories. In several of the graphs the END results are identified as END-SD-FGWP, which stand for Electron-Nuclear Dynamics with a Single Determinant for the electrons and a Frozen Gaussian Wave Packet for the nuclei taken in the limit of narrow width. This is the level of END theory at which the numerical calculations have been performed.

In Fig. 5 the differences in the scattering angles of the bare nuclei and the hydrogen-atom potential relative to the END results are shown.

It is clear from this figure (Fig. 5) that the errors due to prescribed trajectories can be quite large for small impact parameters. From Fig. 4 it can be seen that the dynamical trajectory lies between the bare nuclear and the hydrogen-atom potentials. This is due to the fact that, in the $H^+ + H$ system, charge transfer is expected; so the interaction potential should be represented by a combination of the bare nuclei and the atomic potential. The contribution of each extreme potential (bare nuclei and atomic) is related to the amount of charge transfer during the collision and cannot be predetermined. Consequently, the use of prescribed trajectories in calculating properties that depend upon the scattering angle becomes doubtful for energies below 1 keV and for small impact parameters.

2. Proton-helium collisions

The behavior of proton-helium scattering is different from that of the proton-hydrogen collisions. The $H^+ + He$ system exhibits electron-electron interaction, the charge transfer is nonresonant, and the interaction potential has repulsive and attractive parts. These facts make the scattering of a proton by a helium atom an important system to study with any new time-dependent method that has demonstrated the ability to describe the $H^+ + H$ collision well.

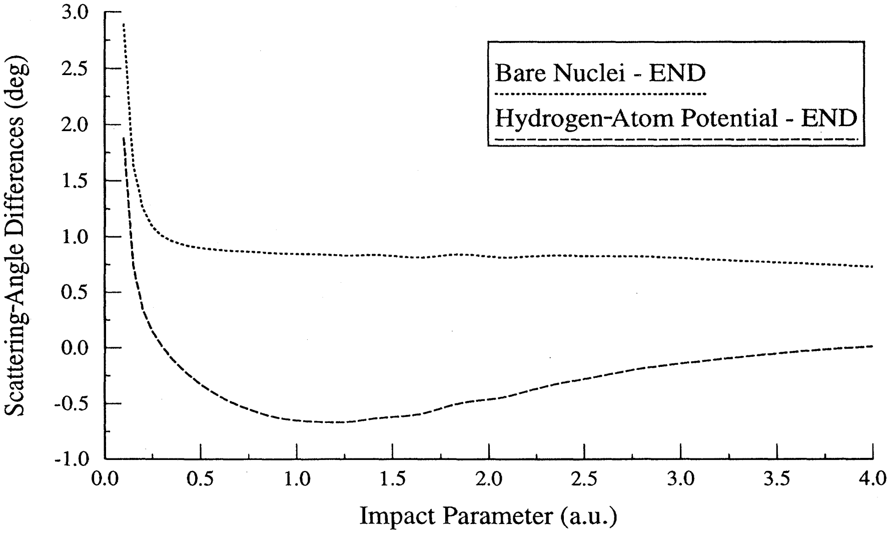

FIG. 5. Scattering-angle differences as a function of impact parameter. Bare nuclei and hydrogen-atom potential are relative to END results for $H^+ + H$ system. Energy: 500 eV. Basis set: *p*VDZ. Scattering-angle differences in degrees and impact parameter in a.u. Dotted line, bare nuclei–END; dashed line, hydrogen-atom potential–END.

Since the early 1930s proton-helium scattering has been studied by theoretical methods (Kimura, 1985b). The accumulated theoretical data fall mostly in the energy range above 10 keV and are related mainly to total (integral) cross sections. Experimental and theoretical studies of differential cross sections for $H^+ + He$ are more scarce. However, it is possible to find several experimental studies for energies down to 5 keV and scattering angles greater than 1° (Fitzwilson and Thomas, 1972). These experiments are probing the repulsive part of the interaction potential, and no structures are then observed. Recent studies of angular differential scattering at keV energies in ion-atom collisions have focused on very small angles, in general, below 1° (Johnson *et al.*, 1989). These studies are motivated by the highly forward-peaked character of the cross sections and by the location of the classical rainbow angle within the 0°–1° range (at keV energies). The fact that structures occur for very small angles has been the main reason for the delay in investigating this region, since high angular resolution is needed. From the theoretical point of view, the oscillatory patterns seen in elastic and inelastic scattering have been studied extensively using semiclassical theory (McDowell and Coleman, 1970; Maitland *et al.*, 1981; Newton, 1982).

The appearance of classical rainbow scattering implies that the classical deflection function has at least one extremum. This means that there are at least two impact parameters that will yield the same scattering angle. A proton colliding with a helium atom is an example of when three dynamical trajectories can yield the same scattering angle (see Fig. 6).

In general, the deflection function of an ion-atom system has at least one extreme point. The exception is the resonant collision of a proton with a hydrogen atom. This behavior of the deflection function is due to the interaction potential, which for the nonresonant case has both repulsive and attractive parts. The deflection function is presented for the $H^+ + He$ system at 50.0 eV. At this energy, the elastic scattering is the only important process. Consequently, classical elastic-scattering theory can be used to invert the deflection function to yield the intermolecular potential. Although the results are not shown here, this potential has been obtained from the electron-nuclear dynamics (END) results and compared to the dynamic potential and to the Born-Oppenheimer potential-energy surface with essentially perfect fit (Longo, 1993). The deflection function is shown in Fig. 6.

The classical differential cross section for $H^+ + He$ at 500 eV illustrates the power of the END approach. Calculations have been performed with equally satisfactory results for various collision energies up to 5 keV. Since the differential cross section depends upon the deflection function, the three regions of the deflection function are given in Fig. 7. The regions are (I) $\{0, b_0\}$, where b_0 corresponds to the value of the impact parameter for which the deflection function vanishes, the so-called glory angle, $\Theta(b_0)$; (II) $\{b_0, b_r\}$, where b_r defines the rainbow angle, that is, the extremum of the deflection function for which $d\Theta(b)/db|_{b=b_r} = 0$; and (III) $\{b_r, \infty\}$, the attractive region.

As stated before, from the shape of the deflection function in Fig. 7 it can be seen that more than one impact parameter leads to the same scattering angle θ. Thus, the equation for the classical differential cross section becomes

$$\sigma_d = \frac{d\sigma}{d\Omega} = \sum_i \frac{b_i P(b_i)}{\sin\theta |d\Theta/db|_{b=b_i}} , \tag{4.5}$$

i.e., a sum of contributions from these different trajectories. The contributions of each one of the three regions for the elastic and for the charge-transfer differential cross sections are shown in detail in Figs. 8 and 9.

The value of the rainbow angle θ_r can be determined

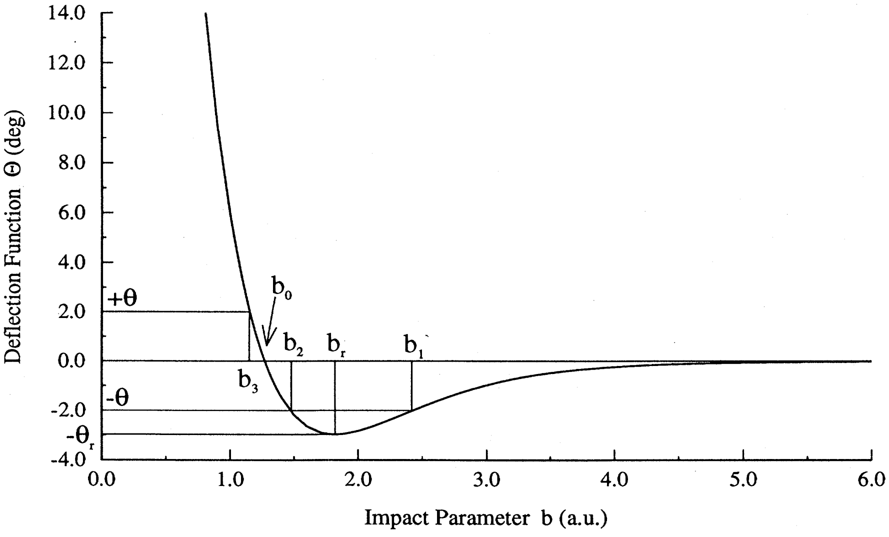

FIG. 6. Deflection function for $H^+ + He$. END results are at 50.0 eV with a *p*VDZ basis set.

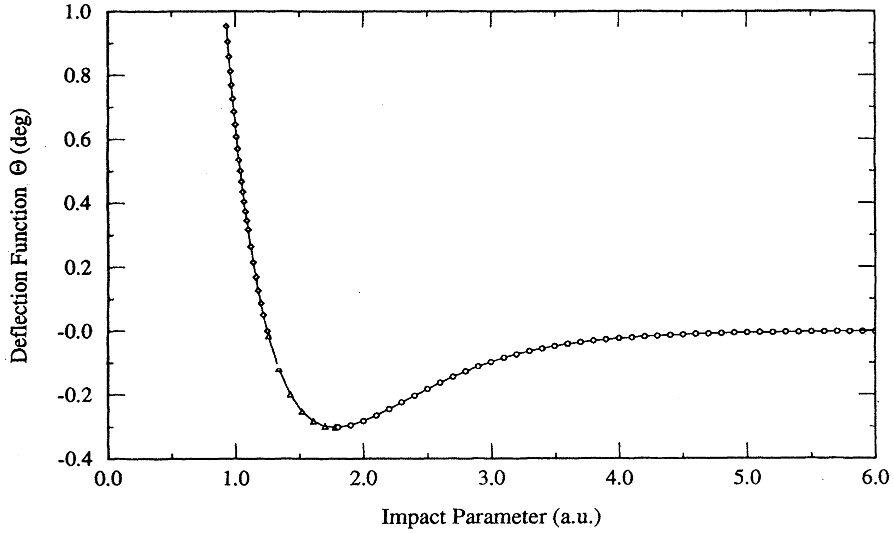

FIG. 7. Deflection function for $H^+ + He$. END results are at 500 eV with a *p*VDZ basis set. Regions: (I) ◇; (II) △; (III) ○.

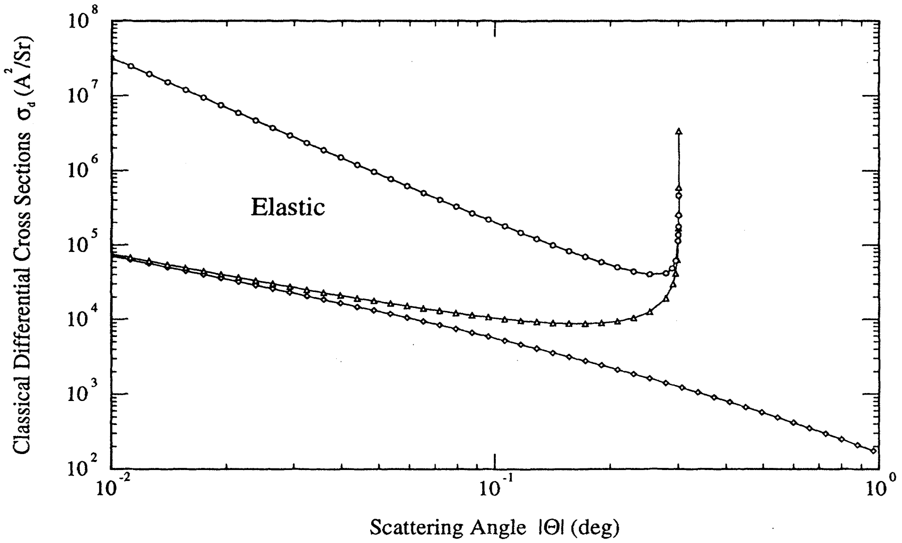

FIG. 8. Elastic differential cross section for $H^+ + He$. END results are at 500 eV with a *p*VDZ basis set. Regions: (I) ◇; (II) △; (III) ○.

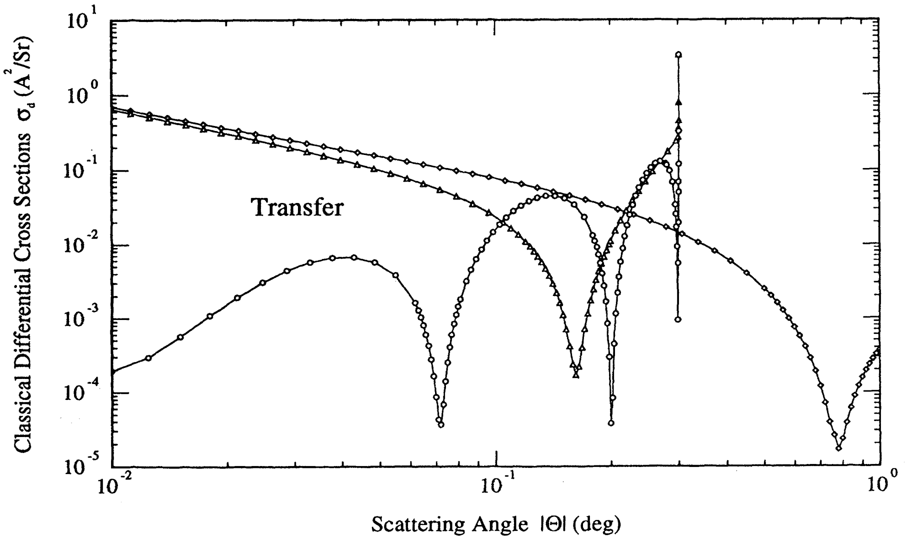

FIG. 9. Charge-transfer differential cross section for $H^+ + He$. END results are at 500 eV with a *p*VDZ basis set. Regions: (I) ◇; (II) △; (III) ○.

TABLE V. Experimental and theoretical rainbow angles for the $H^+ + He$ system.

Energy (eV)	Rainbow angle (deg) Experimental[a]	END	Impact parameter (a.u.) END
50.0		2.963	1.826
500	0.32	0.3015	1.778
1500	0.11	0.1013	1.772
5000	0.03	0.0302	1.772

[a] Johnson *et al.* (1989).

experimentally as the position of the inflection in $\sigma_d(\theta)$ beyond the rainbow maximum. For the scattering of a proton with a helium atom, the experimental determination of the rainbow angle is compared with the theoretical result in Table V. The agreement is excellent between the END results and the experimental rainbow angles.

The range of 0.01°–1.0° and $0.04° < (kb)^{-1} < 0.29°$ for $H^+ + He$ at 500 eV, i.e., the region of very small angles, which means $\theta \le (kb)^{-1} \simeq 0$, is considered. A classical elastic cross section will not yield correct results near the rainbow angle. Semiclassical corrections to the classical cross sections can be used (Berry, 1966; Smith, 1969; Longo, 1993). The elastic differential cross section obtained with ENDyne and semiclassical corrections is shown in Fig. 10.

The results for 500 eV are presented, since at this energy the elastic process is several orders of magnitude larger than the charge transfer. Thus the semiclassical corrections to the classical elastic differential cross section are adequate, as can be seen from the comparison between the theoretical and the experimental results. An appropriate formalism within END that will yield quantum interferences for inelastic processes remains to be developed.

C. Ion-molecule scattering

There are surprisingly few rigorous theoretical investigations of the dynamics of ion-molecule collisions in the low- to intermediate-energy regime (50 eV $< E <$ 50 keV) (Kimura, 1985a). There are likely several reasons for this lack of theoretical treatment, not the least being the complexity and cost of obtaining reasonably accurate adiabatic potentials and eigenstates as functions of internuclear distances and molecular orientations. In addition, for an ion-molecule system, the number of internal degrees of freedom that need a proper dynamical treatment increases dramatically. The END theory in this context fills a need, since it does not need adiabatic potentials and treats properly all degrees of freedom.

The performance of the END theory for ion-molecule collisions is examined in this section, as exemplified by the system $H^+ + H_2$. In these types of collisions not only do the electrons play an important role (transfer and excitation), but so do the nuclei, since vibrational and rotational excitations take place.

The END results are discussed for the collision of a proton with H_2 (in its electronic and vibrational ground state) at a collision energy of 500 eV. Three molecular orientations are studied, namely, (0°, 0°), (45°, 0°), and (90°, 0°). These are representative of the effects of orientation of the target molecule on the charge-transfer mechanism, cross sections (charge transfer), and energy-transfer mechanisms. The same notation as that of Kimura (1985a) is used for the molecular orientation (α,β). The first angle, α, is the angle between the scattering direction and the molecule axis, and β is the dihedral angle between the scattering plane and the molecular plane.

The nuclear motion of an ion-molecule collision is quite a bit more complicated (and more interesting) than that of ion-atom scattering, since, in ion-molecule collisions, one expects vibrational and rotational excitations

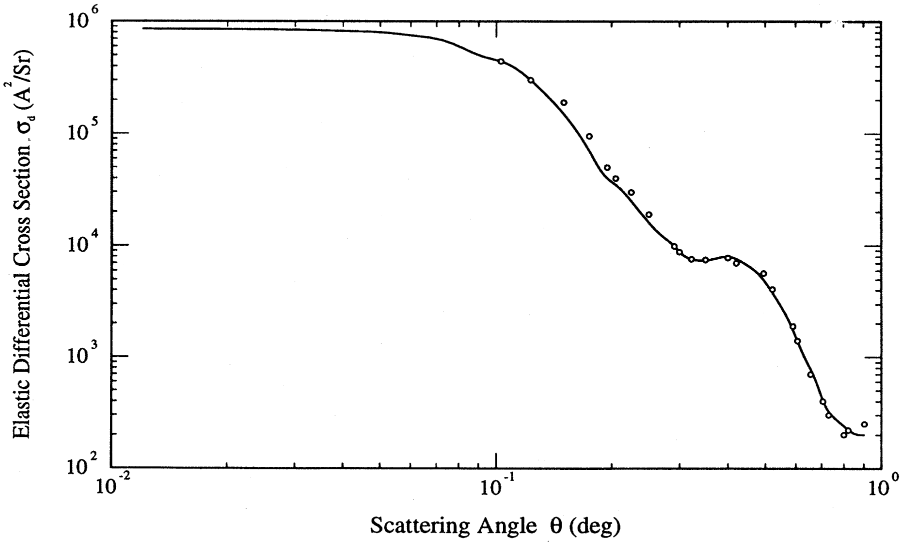

FIG. 10. Elastic differential cross section for $H^+ + He$. Energy: 500 eV. Basis set: *p*VDZ. The solid line corresponds to the semiclassical corrections to the END results. The circles are experimental data (Johnson *et al.*, 1989).

to occur. The angular dependence of the vibrational populations of the H_2 molecule after a collision with H^+ has been studied by theoretical and experimental methods for low ($E < 30$ eV) and high energies ($E > 10$ keV). In the intermediate-energy range (100 eV $< E <$ 10 keV) experimental results for differential vibrationally resolved $H^+ + H_2$ scattering have been obtained only recently and are already challenging the theory (Dhuicq and Benoit, 1991). Our classical description of the nuclear motion has to be augmented by some approximate vibrational wave function in order to yield the angular dependence of the vibrational populations of H_2. Here only the vibrational analysis of the classical motion of the nuclei is presented.

The preferred way to obtain vibrational frequencies of the H_2 target is to use the Prony method (Marple, 1987) in the analysis of the interatomic distance of the H_2 molecule as a function of time. The Prony method is an alternative to the discrete Fourier transform for spectral analysis and is widely used in signal processing. It is a technique for modeling sampled data as linear combinations of (complex) exponentials with damping coefficients ε and angular frequencies ω, i.e.,

$$x(n) = \sum_{l=1}^{p} h_l e^{-(\varepsilon_l + i\omega_l)n(\delta t)} , \tag{4.6}$$

where the number of terms p is called the order of the method, and the equally spaced steps of the data sample are $n(\delta t)$. Details of the algorithm and its implementation can be found in the literature (Marple, 1987). Once the parameters of the exponential model are determined, the frequency spectrum can be obtained directly using the infinite domain analytic Fourier transform

$$\tilde{x}(k) = N(\delta t) \sum_{n=0}^{N-1} x(n) e^{-i2\pi kn/N} , \tag{4.7}$$

where N is the number of points in the data sample. In order to enhance the signal, it is useful to use the relative spectral densities (RSD) as a function of the frequency ω to obtain the spectrum. The RSD, expressed in decibel (dB), is defined as

$$\mathrm{RSD}(\omega)[\mathrm{dB}] = 10 \log_{10} \left[\frac{|x(\omega)|^2}{\max|x(\omega)|^2} \right] . \tag{4.8}$$

In Table VI the vibrational frequencies are presented for all trajectories of the (0°,0°), (45°,0°), and (90°,0°) molecular orientations that lead to the same scattering angle (namely, that of 0.29°). The differences in the vibrational states are basically due to differences in the charge and energy transfer and, thus, the electronic state of the H_2 target after the collision.

The range of vibrational frequencies in Table VI indicates the difficulties in obtaining average properties like differential vibrational populations from any state-to-state procedure. With the present implementation of the END theory, one could proceed by finding an appropriate nuclear wave function to calculate the vibrational populations and also average with respect to the molecular orientations. Table VI also shows that for each initial condition (impact parameter and molecular orientation) the resulting vibrational frequency of the H_2 target is distinct, which implies that it is in a different time-dependent electronic state (or rather moving on a different effective dynamical potential curve). These different time-dependent electronic states result from the differences in charge-transfer probabilities for each initial condition, as is suggested by the correlation between the transfer probabilities and the vibrational frequencies. In general, when the H_2 molecule loses electron density, the bond becomes weaker and the vibrational frequency decreases.

The charge transfer in the $H^+ + H_2$ scattering has been studied theoretically by a close-coupling method (Kimura, 1985a) at energies ranging from 200 to 1000 eV. A direct comparison between the ENDyne and the close-coupling results is made for the weighted charge-transfer probability and shown in Fig. 11 for the (0°,0°) molecular orientation.

The two approaches do not agree. The total charge-transfer cross section is 1.562×10^{-18} cm^2 for the close-coupling method (Kimura, 1956a) and 1.287×10^{-17} cm^2 for the END-SD-FGWP method. The differences might be explained by the assumptions and approximations

TABLE VI. Vibrational frequencies (cm^{-1}) of H_2 after collision with H^+ at 500 eV as a function of the initial conditions [impact parameter (a.u.) and molecular orientation ($\alpha°,\beta°$)].

b (a.u.)	($\alpha°,\beta°$)	Charge transfer Probability ($\times 10^{-2}$)	Vibrational frequency (cm^{-1})
2.160	90,0	5.418	4425
1.251	0,0	3.209	4441
1.593	0,0	2.473	4467
1.516	45,0	2.925	4497
1.886	45,0	0.899	4547
3.449	90,0	0.689	4561
3.446	45,0	0.342	4599
3.420	0,0	0.289	4612
1.731	90,0	0.134	4642

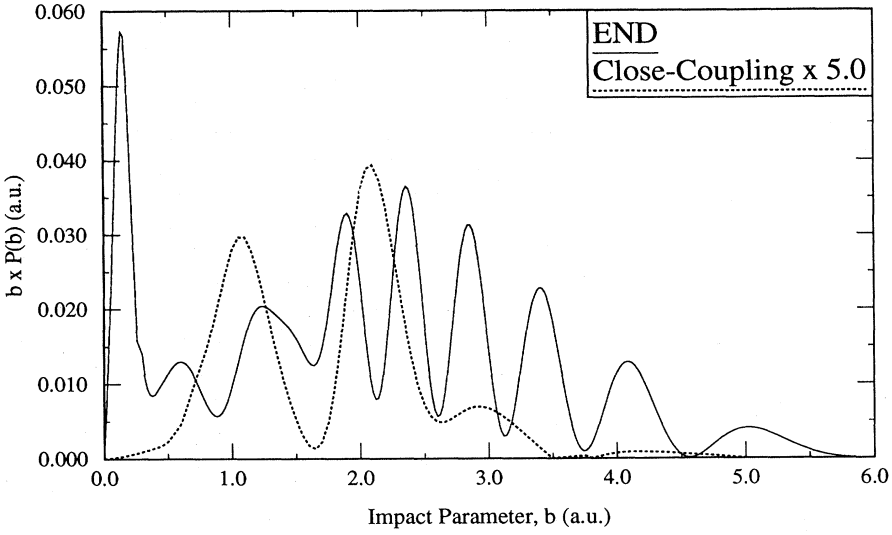

FIG. 11. END and close-coupling (Kimura, 1985a) results for the weighted charge-transfer probability in the $H^+ + H_2$ collision at 200 eV in the (0°,0°) orientation. The solid line corresponds to the END results; the dotted line, to close-coupling ones.

adopted by each method. In the case of close coupling, the nuclear dynamics is described by a prescribed trajectory, which limits its applicability for low collision energies. Moreover, the electronic wave function in the close-coupling approach is obtained using the diatoms-in-molecule method, which is less reliable at small to intermediate internuclear separations. The impulse approximation, which freezes the target nuclei during the collision, obviously also introduces errors. This might explain the lack of structure in the close-coupling results at small impact parameters. This particular implementation of the close-coupling method (Kimura, 1985a) includes the effects of electron translation factors, which are only treated approximately in the END formalism. However, at 200 eV collision energy, such effects should not be significant.

It should also be noted that the END method provides results for the differential cross sections (elastic and transfer) for the $H^+ + H_2$ collision at 500 eV in excellent agreement with experimental data (Longo, 1993; Longo *et al.*, 1993).

D. Intramolecular electron transfer

The dynamics of inter- and intramolecular charge transfer has been a very important subject in chemical physics (Chance *et al.*, 1979; DeVault, 1984; Hopfield *et al.*, 1988; Beratan *et al.*, 1990; Newton, 1991). The main reason is that charge transfer is the essence of many fundamental biological and biochemical processes. In addition, charge transfer is important in a variety of fields, such as atomic physics, plasma physics, astrophysics, semiconductor physics, organic and inorganic chemistry, and many others.

In this section the charge-transfer system Li—H-$Li^+ \rightleftharpoons Li^+$-H—Li is studied as a simple model of intramolecular charge transfer using time-dependent methods. This molecular system represents a good prototype for theoretical studies of charge-transfer dynamics, as it is small enough to be treated with some high-level *ab initio* time-dependent and time-independent methods.

Due to its conceptual simplicity, the formalism for electron transfer proposed by Marcus (1956, 1965; Marcus and Sutin, 1985; Newton, 1991) in the late '50s has drawn much attention from both theoreticians and experimentalists. This theory has been extensively reviewed, revised, and extended. However, two basic assumptions are still being employed, namely, (a) that there is a reaction coordinate that takes the reactants to the products via nuclear motion, and (b) there is a coupling (H_{12}) between two electronic states (donor and acceptor). A typical electron-transfer reaction coordinate is shown in Fig. 12.

Nondynamical-type approaches for electron transfer assume that the transfer rate k is usually given by an equation based on Fermi's golden rule (Marcus and Sutin, 1985; Newton, 1991; Evenson and Karplus, 1992),

$$k = \frac{2\pi}{\hbar} |H_{12}|^2 (\mathrm{FC}) . \qquad (4.9)$$

The quantity (FC) is the Franck-Condon factor and is related to the vibrational spectrum of the donor-acceptor system and its surroundings, if any. Analytical expressions for (FC) derived from classical and semiclassical theories exist and are discussed in the references (Marcus and Sutin, 1985; Newton, 1991). The matrix element H_{12} represents the electronic coupling of the donor and acceptor (or reactant and product). This is the quantity that has been challenging theoreticians and experimentalists. There are several approaches to computing the electron-transfer-matrix element. Usually, for large systems such as proteins, the transfer dynamics is treated as a one-electron problem (Beratan *et al.*, 1990; Evenson and Karplus, 1992). However, for small molecular systems, many-electron *ab initio* and semiempirical methods have been used (Newton, 1991). In this case, the most common approach to calculating H_{12} is to compute the

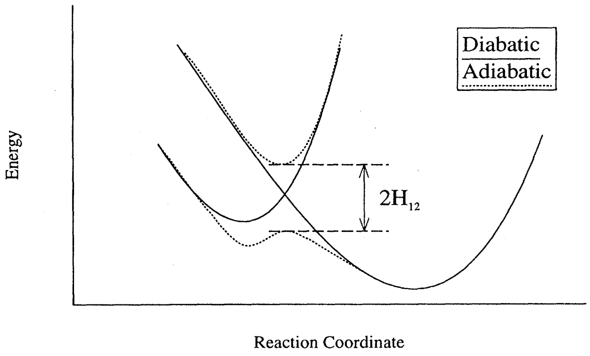

FIG. 12. Diabatic and adiabatic potential curves for normal electron transfer.

diabatic states, which in general are nonorthogonal, and either use them as zero-order states in a perturbational approach (Ohta *et al.*, 1986; Newton, 1991) or use them in a two-dimensional nonorthogonal configuration-interaction problem (Jackels and Davidson, 1976; Broo and Larsson, 1990). More specifically, the broken space symmetry wave functions, $|1\rangle$ and $|2\rangle$, are used in the following equation for the coupling element (Newton, 1980; Ohta *et al.*, 1986; Broo and Larsson, 1990; Newton, 1991),

$$H_{12}=\frac{1}{1-S_{12}^2}\left|\langle 1|H|2\rangle - S_{12}\frac{\langle 1|H|1\rangle+\langle 2|H|2\rangle}{2}\right| , \qquad S_{12}=\langle 1|2\rangle . \tag{4.10}$$

Since the nuclear motion is responsible for electron transfer (Newton, 1980, 1991), attempts have been made to treat the motion of the nuclei explicitly. Most of these dynamical approaches are also two-state models with a coupling H_{12}. One of these approaches uses an *ab initio* method to calculate the coupling H_{12} at each nuclear configuration as the system is evolving in time (Mikkelsen *et al.*, 1987; Mikkelsen and Ratner, 1989). Some simpler approaches use a model potential function for the electronic state, and the nuclear motion is treated explicitly either by the time-dependent variational principle (Deumens *et al.*, 1987a) or by the semiclassical approach of Nikitin (Larsson, 1981). All these approaches for electron transfer require the calculation of the coupling matrix element. In order to obtain H_{12}, it is necessary to know the reaction coordinate, and that might be very difficult to determine for large systems.

Another approach would be to use an extension of the variational transition-state theory, with or without semiclassical corrections for tunneling (Gonzalez-Lafont *et al.*, 1991; Melissas *et al.*, 1992), to include the most important electronic wave-function parameter as a reaction coordinate. The minimum-energy path around which the transition-state theory is formulated is then defined in a configuration space that includes the electronic degrees of freedom. The END theory reviewed here constructs dynamical paths in the phase space, including electronic degrees of freedom, and computes the transition probability from it. The main advantage is that one does not need to break the transfer into two separate steps, i.e., geometry change and electronic transition, but can describe the full evolution of the interaction between both these aspects of the process. To initialize the electron transfer, one simply distorts the molecule and lets the system evolve in time.

The basis set used is 3–21G+ for Li (Clark *et al.*, 1983) and 3–21G for H (Binkley *et al.*, 1980). The time-independent calculations are performed by ACES II program system (Stanton *et al.*, 1992). The time-dependent results are obtained by the ENDyne program. The initial conditions for the time-dependent calculations are obtained as follows: (a) The longer Li—H bond is stretched and the shorter Li-H bond compressed by the same percentage (%) amount; (b) a SCF time-independent calculation is performed on this new structure; and (c) the converged SCF vectors are used as the initial electronic parameters z for the time-dependent calculation. The evolution was propagated up to 10 000 a.u. of time (≈ 0.24 ps).

The global minimum of the LiHLi molecule is a bent C_{2v} structure. However, the linear structure presents an unrestricted Hartree-Fock (UHF) broken-symmetry solution, with two charge localized structures: $\mathrm{Li}^{(0)}$—H-$\mathrm{Li}^{(+1)} \rightleftharpoons \mathrm{Li}^{(+1)}$-H—$\mathrm{Li}^{(0)}$. These linear charge-transfer structures are considered, and the structure and energies of the two symmetric minima are shown in Table VII.

As mentioned before, the initial conditions for the evolution of the charge transfer are chosen by contracting and stretching the Li-H bonds. Table VIII summarizes the energetics of the initial conditions studied. The Boltzmann factor (BF) in Table VIII is calculated as

$$\mathrm{BF}=e^{-\Delta E/kT}=e^{-503.22395\Delta E/T} \tag{4.11}$$

with ΔE given in kcal/mol and T in K.

The value of 1450 K corresponds to the temperature at

TABLE VII. Linear LiHLi properties. UHF/3-21G+/Li//3-21G/H.

Li(1)-H = 3.09017 a.u.
H-Li(2) = 3.45561 a.u.
E(SCF) = −15.33537897 a.u.
Average multiplicity = 2.0000660
Harmonic frequencies (cm^{-1}): 98.9i (Π); 368.5 (Σ^+); 1631.5 (Σ^+)
Zero-point vibrational energy = 2.8592 kcal/mol

TABLE VIII. Initial conditions for the time-dependent calculations.

Structure	Li(1)-H (a.u.)	Li(2)-H (a.u.)	Energy −15.0+ (a.u.)	ΔE (kcal/mol)	BF	
					$T=300$ K	$T=1450$ K
Equil.	3.090	3.455	−0.335379	0.0		
5.6%	2.917	3.649	−0.333829	0.973	0.1955	0.7134
10%	2.781	3.801	−0.330281	3.200	4.665(−3)	0.3294
13%	2.688	3.905	−0.326528	5.554	8.994(−5)	0.1455
15%	2.611	3.974	−0.322588	8.027	1.420(−6)	0.06168
18%	2.534	4.077	−0.317466	11.242	6.361(−9)	0.02021
20%	2.472	4.147	−0.312707	14.227	4.323(−11)	0.007172

which the thermal energy ($kT=2.9$ kcal/mol) is the same as the zero-point vibrational energy or half a vibrational quantum. It is reasonable to assume that the electron transfer triggered by molecular vibrations should be induced by thermal energy, and this temperature gives some sense of the relation between temperature and vibrational excitation. At room temperature only small vibrational excitations of the system are expected.

A time-dependent calculation generates a lot of data, since the whole history of the evolving system is recorded. Only some selected properties are presented here as they evolve in time. The nuclear motion is shown evolving in time as a function of the distortion from the equilibrium structure. These results give some idea of the time scale of the nuclear motion which can be compared to the time scale of some other properties. For clarity, instead of the nuclear coordinates, Fig. 13 shows the time evolution of the Li(1)-H and H—Li(2) bond distances for 5.6%, 10%, and 18% deformation.

The alpha and beta Mulliken populations (the alpha spins are arbitrarily in excess in the chosen single-determinant state) as a function of time are also presented. The results for the 10% displacement are shown in detail, since, among all the studied initial conditions, it gives the greatest variation of the beta population. Figures 14 and 15 contain the alpha and beta populations of H, Li(1), and Li(2) atoms, respectively.

As can be seen from the figures, the variation of the beta population is very small compared to the variation of the alpha population on the lithium atoms. As a result, the system can be considered as being an effective one-electron system. In Fig. 16 the alpha Mulliken population (Szabo and Ostlund, 1989) is shown on Li(2) for all initial conditions considered here.

To derive a transfer-rate constant from the quantum-mechanical results, an ensemble of LiHLi molecules (in the linear structure) is considered and a Boltzmann distribution is applied. For a given initial state n, the wave function of the LiHLi (linear) molecule evolves in time (t) with a probability for electron transfer given by $P_n(t)$. As a result, assuming that at time zero ($t=0$) there is no product present, the rate of consumption of the reactant is given by

$$\frac{dX(t)}{dt}=-k_{\mathrm{ET}}X(t)\ , \tag{4.12}$$

where $X(t)$ is the reactant concentration as a function of time, and k_{ET} is the electron-transfer-rate constant for a first-order kinetics. The connection between electron-transfer probability and reactant concentration is made

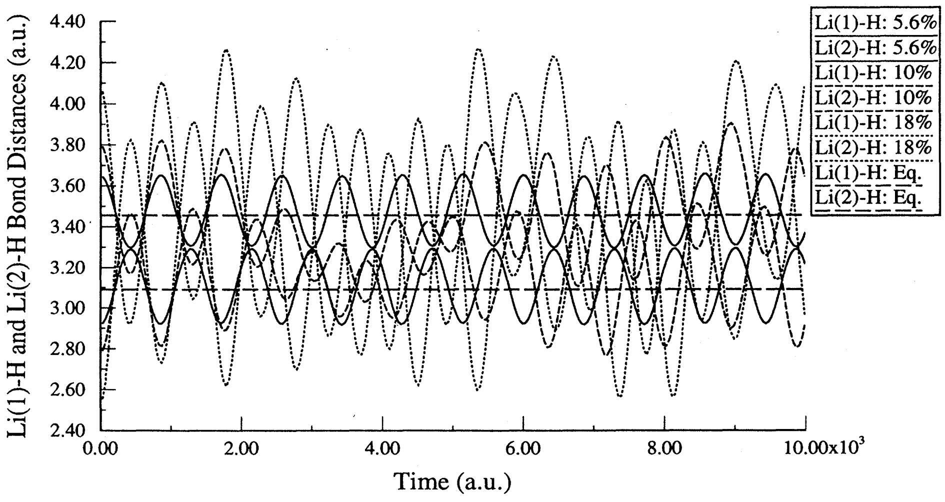

FIG. 13. Li(1)-H and Li(2)-H bond distances (a.u.) as a function of time (a.u.) for 5.6%, 10%, and 18% displacements.

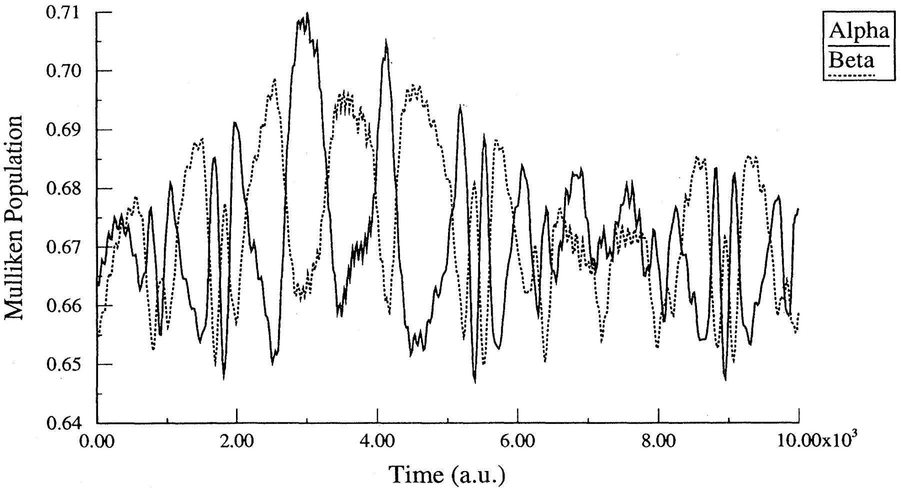

FIG. 14. Alpha and beta Mulliken populations on H for 10% displacement.

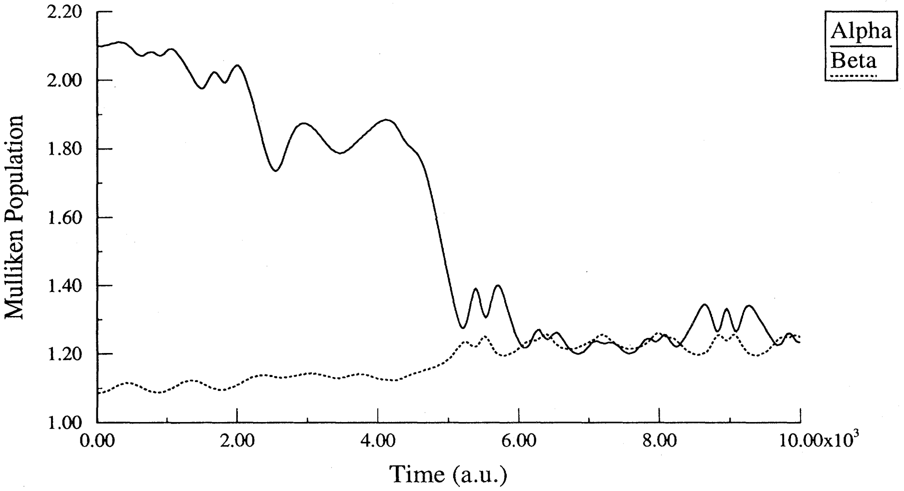

FIG. 15. Alpha and beta Mulliken populations on Li(2) for 10% displacement.

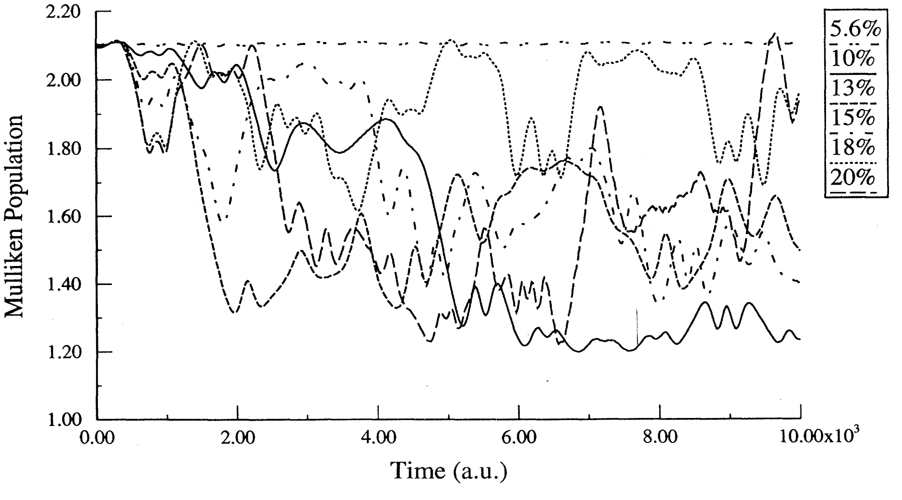

FIG. 16. Alpha Mulliken population on Li(2) for 5.6%, 10%, 13%, 15%, 18%, and 20% displacements.

via statistical mechanics using the Boltzmann distribution at a given temperature for all possible initial conditions, i.e.,

$$X(t)=\sum_n e^{-E_n/kT}P_n(t)\ . \tag{4.13}$$

The integration of the first-order-kinetics equation gives

$$\frac{dX(t)}{X(t)}=-k_{\mathrm{ET}}dt \Longrightarrow \ln X(t)=-k_{\mathrm{ET}}t\ , \tag{4.14}$$

so that the logarithm of the concentration should be linear with time.

As mentioned before, the electron transfer in the LiHLi molecule is effectively a one-electron event. Since, for a one-electron system, the transfer probability and the Mulliken population are identical, the probability for electron transfer can be approximated by

$$P_n(t)=2-2M_n(t)/M_n^{\max}\ , \tag{4.15}$$

where M_n is the alpha Mulliken population on Li(2) for initial condition n, and $M_n^{\max}$ is the maximum value of this population. This equation means that the Mulliken population is normalized to maximum two full electrons and the complement taken to get a number between 0 and 1 as the probability that an electron will move from Li(2) to Li(1), signifying a charge-transfer event. For this study, which is only illustrative, the ensemble is restricted to include only the initial conditions ($n=6$) involving the bond-length distortions of 5.6%, 10%, 13%, 15%, 18%, and 20%. The Boltzmann factors at room temperature for each initial condition are presented in Table VIII. In Fig. 17 the concentration is given as a function of time within this simple model.

The small statistical sample leaves strong fluctuations on the time scale of the nuclear vibrations. This is, of course, what should be expected and is typical of any detailed microscopic dynamics entered as data for a statistical treatment to reveal macroscopic quantities. However, the simple exponential expected from first-order kinetics to the data can readily be fitted and gives a limiting concentration of 0.005 and a rate constant of 0.0003 a.u., which is $1.25\times10^{13}\ \mathrm{sec}^{-1}$ at 300 K.

No experimental results exist for LiHLi; so this example serves only to illustrate the theoretical approach to obtain rate constants from detailed dynamical calculations.

V. DISCUSSION

In this section, some general aspects of time-dependent treatments are discussed. The basic conservation laws and symmetries of molecular quantum mechanics serve as the starting point.

A. Invariance principles

Laboratory-fixed coordinate axes are employed and describe the nuclear degrees of freedom in Cartesian form. This means that the dynamics includes the overall translational and rotational motion, which then have to be separated out whenever necessary. The time-dependent variational principle (TDVP) has conservation laws (Kerman and Koonin, 1976; Negele and Orland, 1988; Broeckhove *et al.*, 1988, 1989a, 1989b) associated with it, somewhat like Noether's theorem (Noether, 1981; Goldstein, 1980). It allows the derivation of the total linear and angular momentum as constants of the motion, provided the manifold of states considered is invariant under the symmetry operations associated with the conservation laws. Stated somewhat differently, the TDVP equations have a rigorous conservation law when the Poisson bracket of the expectation values of a conserved operator and the energy equals the expectation value of the commutator of that operator with the quantum-mechanical Hamiltonian. The existence of the conservation laws makes it possible to avoid all transformations to internal coordinates. All time-dependent formulations that keep a strict connection to the

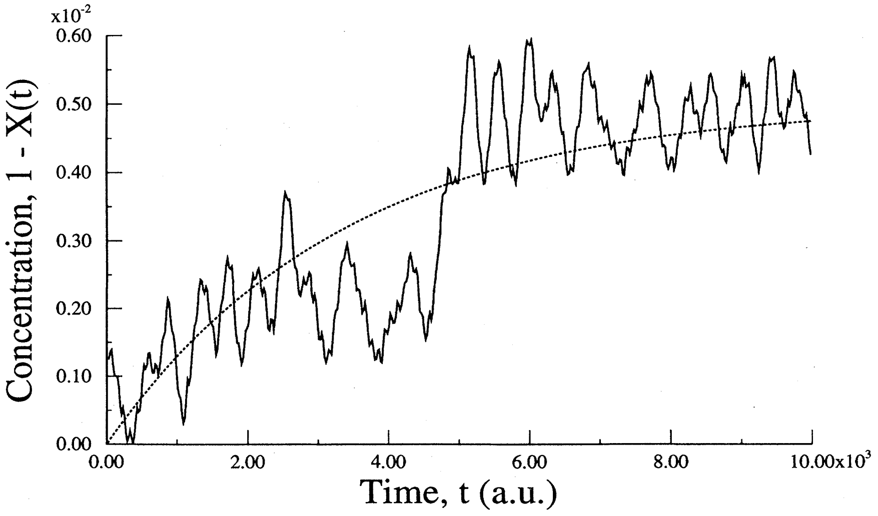

FIG. 17. Concentration of the product as a function of time. The smooth curve is an exponential fitted visually to the dynamical curve. The exponential has a limiting concentration of 0.005 and a rate of 0.0003 a.u.

Schrödinger equation or the underlying variational principle like END (Deumens, Diz, Taylor, and Öhrn, 1992) and Theilhaber's time-dependent density-functional (TDDF) theory (Theilhaber, 1992) have the correct conservation laws.

To avoid confusion in the derivatives, it is important to understand what is meant by a function lying in the manifold of TDVP variations. One says that $|\delta\zeta\rangle$ lies in the manifold of TDVP variations if it is in the tangent plane of the manifold. It may not be possible to write a variation of the wave function in terms of the basis set being used, yet it belongs to the manifold of TDVP variations. For example, consider the trivial case of a hydrogen atom in translational motion, i.e., a single-electron state, using a truncated basis with a single 1*s* function moving with the nucleus. Then $\delta\phi=\phi_{1s}(\mathbf{r},\mathbf{R}+\delta\mathbf{R})-\phi_{1s}(\mathbf{r},\mathbf{R})$ is, in the limit, a function with *p* symmetry and lies in the *tangent* space of the manifold, but outside the manifold derived from this limited basis.

The use of this property in derivations is common. For instance, an expression such as $\langle\delta\zeta|i(d/dt)\zeta\rangle$ may be replaced by $\langle\delta\zeta|H|\zeta\rangle$ if and only if $|\delta\zeta\rangle$ lies in the tangent plane (see Broeckhove *et al.*, 1988, 1989a, 1989b).

1. Translation invariance in time

Let us first consider the (almost trivial) conservation of energy. From the Hamiltonian structure of the TDVP equations it follows that

$$\frac{dE}{dt}=\{E,E\}=0\ . \tag{5.1}$$

Furthermore, it is obvious that the time derivative of the wave function, by construction, lies in the manifold of states over which the TDVP variations are carried out. Therefore

$$\begin{aligned}\frac{d}{dt}\langle\zeta|H|\zeta\rangle&=\langle(d/dt)\zeta|H|\zeta\rangle+\langle\zeta|H|(d/dt)\zeta\rangle\\&=\langle\delta\zeta|H|\zeta\rangle+\langle\zeta|H|\delta\zeta\rangle\\&=i\hbar\langle\delta\zeta|(d/dt)\zeta\rangle-i\hbar\langle(d/dt)\zeta|\delta\zeta\rangle\\&=i\hbar\langle(d/dt)\zeta|(d/dt)\zeta\rangle\\&\quad-i\hbar\langle(d/dt)\zeta|(d/dt)\zeta\rangle\\&=0\ .\end{aligned} \tag{5.2}$$

The same result is obtained for the energy viewed either as the value of the Hamiltonian function in the generalized phase space or as the expectation value of the quantum-mechanical Hamiltonian operator. Thus energy is conserved.

2. Translation invariance in space

Conservation of total linear momentum is satisfied for a truncated basis set as long as the basis functions are centered on the moving nuclei. If the basis functions are fixed in space, then a complete set is needed before momentum is conserved by the equations of motion. This section analyzes in detail the case of a classical description of the nuclei and the basis functions centered on them without electron translation factors. Thus all metric terms of the form $C_{\mathbf{P}}$, $C_{\mathbf{PP}}$, $C_{\mathbf{RP}}$, and $C_{\mathbf{PR}}$ vanish in Eq. (3.36).

Since the electronic basis functions depend on the nuclear and electronic positions, and do so in the form $\mathbf{r}_i-\mathbf{R}_k$, one finds

$$\frac{1}{i}\left[\sum_{k=1}^{N_{\rm nuc}}\nabla_{\mathbf{R}_k}+\sum_{n=1}^{N}\nabla_{\mathbf{r}_n}\right]|z\rangle=0\ . \tag{5.3}$$

Thus

$$\sum_{n=1}^{N}\nabla_{\mathbf{r}_n}|z\rangle=-\sum_{k=1}^{N_{\rm nuc}}\nabla_{\mathbf{R}_k}|z\rangle\ . \tag{5.4}$$

The expectation value of the total momentum is

$$\begin{aligned}\mathbf{P}_{\rm tot}&=\sum_k\mathbf{P}_k+\mathbf{p}_{\rm el}\\&=\sum_k\mathbf{P}_k+\langle z|\frac{1}{i}\sum_n\nabla_{\mathbf{r}_n}|z\rangle/\langle z|z\rangle\ ,\end{aligned} \tag{5.5}$$

and its time derivative is

$$\begin{aligned}\dot{\mathbf{P}}_{\rm tot}&=\sum_k\dot{\mathbf{P}}_k+\dot{\mathbf{p}}_{\rm el}\\&=\sum_k\dot{\mathbf{P}}_k+\frac{d}{dt}(\langle z|\frac{1}{i}\sum_n\nabla_{\mathbf{r}_n}|z\rangle/\langle z|z\rangle)\ .\end{aligned} \tag{5.6}$$

The latter is expanded in terms of the parameters, in particular,

$$\frac{d}{dt}\frac{\langle z|\frac{1}{i}\sum_n \nabla_{\mathbf{r}_n}|z\rangle}{\langle z|z\rangle}=\sum_i \dot{z}_i^*\frac{\frac{\partial}{\partial z_i^*}\langle z|\frac{1}{i}\sum_n \nabla_{\mathbf{r}_n}|z\rangle}{\langle z|z\rangle}+\sum_i\frac{\langle z|\frac{1}{i}\sum_n \nabla_{\mathbf{r}_n}\frac{\partial}{\partial z_i}|z\rangle}{\langle z|z\rangle}\dot{z}_i$$
$$+\sum_k \dot{\mathbf{R}}_k\frac{\nabla_{\mathbf{R}_k}(\langle z|)\frac{1}{i}\sum_n \nabla_{\mathbf{r}_n}|z\rangle}{\langle z|z\rangle}+\sum_k\frac{\langle z|\frac{1}{i}\sum_n \nabla_{\mathbf{r}_n}\nabla_{\mathbf{R}_k}|z\rangle}{\langle z|z\rangle}\dot{\mathbf{R}}_k$$
$$-\frac{\langle z|\frac{1}{i}\sum_n \nabla_{\mathbf{r}_n}|z\rangle}{\langle z|z\rangle}\left[\sum_i \dot{z}_i^*\frac{\frac{\partial}{\partial z_i^*}\langle z|z\rangle}{\langle z|z\rangle}+\sum_i\frac{\langle z|\frac{\partial}{\partial z_i}|z\rangle}{\langle z|z\rangle}\dot{z}_i\right.$$
$$\left.+\sum_k \dot{R}_k\frac{\nabla_{\mathbf{R}_k}(\langle z|)|z\rangle}{\langle z|z\rangle}+\sum_k\frac{\langle z|\nabla_{\mathbf{R}_k}|z\rangle}{\langle z|z\rangle}\dot{\mathbf{R}}_k\right]. \tag{5.7}$$

Using the results of Eq. (5.4), ordering some terms and comparing with the metric matrix terms $C_{\mathbf{R}}$ in Eq. (3.37) and $C_{\mathbf{RR}}$ in Eq. (3.38), one can write

$$\frac{d}{dt}\frac{\langle z|\frac{1}{i}\sum_n \nabla_{\mathbf{r}_n}|z\rangle}{\langle z|z\rangle}=-\sum_{l=1}^{N_{\text{nuc}}}\left[\sum_i(iC^{\dagger}_{\mathbf{R}_l i}\dot{z}_i-iC^{T}_{\mathbf{R}_l i}\dot{z}_i^*)+\sum_k^{N_{\text{nuc}}}C_{\mathbf{R}_l\mathbf{R}_k}\dot{\mathbf{R}}_k\right]. \tag{5.8}$$

Then, since $\sum_l^{N_{\text{nuc}}}\nabla_{\mathbf{R}_l}E=0$ because of the invariance of the energy with respect to a global translation of the nuclei when using a basis centered on the nuclei, one obtains from the product of the third row in Eq. (3.36) that

$$\sum_{l=1}^{N_{\text{nuc}}}\left[\sum_i(iC^{\dagger}_{\mathbf{R}_l i}\dot{z}_i-iC^{T}_{\mathbf{R}_l i}\dot{z}_i^*)+\sum_k^{N_{\text{nuc}}}C_{\mathbf{R}_l\mathbf{R}_k}\dot{\mathbf{R}}_k-\dot{\mathbf{P}}_l\right]=\sum_l^{N_{\text{nuc}}}\nabla_{\mathbf{R}_l}E=0\ . \tag{5.9}$$

Thus

$$\sum_k \dot{\mathbf{P}}_k+\frac{d}{dt}(\langle z|\frac{1}{i}\sum_n\nabla_{\mathbf{r}_n}|z\rangle/\langle z|z\rangle)=0\ . \tag{5.10}$$

An interesting result of this analysis is the physical meaning in terms of the rate of change of the electronic momentum that can be inferred for the $C_{\mathbf{R}}$ and $C_{\mathbf{RR}}$ metric terms.

3. Rotational invariance

Rotational symmetry implies conservation of the expectation value of the total angular momentum

$$\mathbf{L}_{\text{tot}}=\sum_k \mathbf{R}_k\times\mathbf{P}_k+\boldsymbol{l}_{\text{el}}+\mathbf{s}_{\text{el}}\ . \tag{5.11}$$

The derivation is analogous to that for total linear momentum and is not presented here.

4. Time-reversal invariance

Time reversibility is defined by Wigner (1959), on p. 325 of his book, as the requirement that the four-step operation—(1) propagate the state ψ_0 in time from time 0 to time t, to $\psi_1=U(0,t;\psi_0)$, (2) apply time inversion to the state (complex conjugation), to get $\psi_2=\psi_1^*$, (3) propagate the state in time for the same period t again $\psi_3=U(0,t;\psi_2)$, (4) apply time inversion to the state $\psi_4=\psi_3^*$—on any state of the system result in the state one starts from, i.e.,

$$\psi_0=\psi_4=U(0,t;\psi_2)^*=U(0,t;U(0,t;\psi_0)^*)^*\ . \tag{5.12}$$

Because it holds for all states, this implies the (nonlinear) operator identity

$$I=U(0,t;U(0,t;.)^*)^*\ . \tag{5.13}$$

In the case of the Schrödinger equation $i\hbar\dot{\psi}=H\psi$, for which the evolution operator is linear $U(0,t;\psi)=U(0,t)\psi=\exp[-(i/\hbar)Ht]\psi$, this implies

$$\psi_0=U(0,t)^{\dagger}U(0,t)\psi_0 \tag{5.14}$$

for all states; hence the evolution operator is unitary $U(t,0)\equiv U(0,t)^{-1}=U(0,t)^{\dagger}$. This latter condition is called *micro reversibility* [see Messiah (1962), p. 674]. It is only meaningful for linear evolution equations like the exact Schrödinger equation. Equation (5.13) expresses unitarity for general nonlinear evolution equations, including nonlinear approximations such as the ones considered in this review.

The scattering operator is a linear operator only when the evolution operator is linear, which in turn requires that the equation be linear. Then, the more widely known formulation of micro reversibility is obtained as

$$|\langle f|S|i\rangle| = |\langle i|S|f\rangle| \,,$$
$$|S_{fi}| = |S_{if}| \,. \tag{5.15}$$

In this form micro reversibility is often referred to as the *principle of detailed balance*.

It is easy to see, and it has been verified numerically with the computer programs, that the END, TDHF, and TDDF equations are time-reversal invariant. However, because they are nonlinear approximations to the exact, linear Schrödinger equation, they are not micro reversible. Hence scattering amplitudes and probabilities computed with these methods do not satisfy Eq. (5.15). Demkov (1963) has proposed a variational principle for the scattering amplitude that does satisfy Eq. (5.15). Gazdy and Micha (1986; Micha and Gazdy, 1987) have implemented a modified version of Demkov's variational principle to obtain scattering amplitudes that are micro reversible. However, this method does not obtain a new, linear, TDHF evolution operator for the system that produces a linear scattering operator, but rather constructs scattering amplitudes from two different TDHF evolutions, one from the initial state forward and the other from the final state backward. The modified Demkov variational principle then gives a scattering amplitude between the two states as an integral over the two trajectories. The reader is referred to the original work (Gazdy and Micha, 1986; Micha and Gazdy, 1987) and the recent paper by Micha and Runge (1992) for details.

B. Conclusion

The TDVP is used to present a unified derivation of the time-dependent methods for the dynamics of electrons and nuclei that go beyond those employing a single potential-energy surface (PES). In order to be specific, the review focuses on a description employing a single-determinantal wave function for the electrons and classical particles for the nuclei. The TDVP is applied to derive dynamical equations for the wave-function parameters, which then become coordinates of a general dynamical system. The physical properties of the parameters that are important for the procedure are emphasized. In addition, in a brief section, the general mathematical theory is discussed that puts these physical properties in the rigorous context of coherent states and Lie groups and lays the foundation for more general implementations.

The equations are first constructed in their simplest mathematical form, which uses an orthonormal reference basis built with nonfollowing atomic orbitals to describe the determinantal wave function. This is the form used by Theilhaber (1992). These are the equations that Car and Parrinello might have formulated instead of introducing fictitious kinetic energies. Then a symplectic transformation is applied to the dynamical equations, in order to obtain a representation in an orthonormal basis built with ordinary AO's, that follow the nuclei, or traveling AO's, with electron translation factors (ETF's). This form of the equations is the natural form for a semiempirical Hamiltonian. The equations introduced by Field are then recovered (Field, 1992) by further assuming that the metric terms coupling the electronic and nuclear degrees of freedom can be neglected.

Applying a second symplectic transformation yields a representation of the equations in the nonorthogonal atomic basis. This makes the method feasible for *ab initio* Hamiltonians, which would otherwise require a very expensive four-index integral transformation of the two-electron integrals each time the numerical integrator takes a step. The nonlinear equations of the density matrix and the close-coupling equations are also derived.

Finally, the solution of the linearized equations is obtained and used to define a third symplectic transformation. This puts the equations in an interaction picture, where the fast oscillations are transformed away. The interaction picture allows the numerical integrator to proceed with large steps, without losing the full nonlinearity of the original equations.

The structure of the equations is brought out and the terms that have been the subject of some debate regarding electron translation factors are analyzed. In order to clarify the physical meaning of ETF's and traveling AO's, molecules in uniform motion are analyzed.

The implementation of the equations in the ENDyne computer software are discussed, and some of the results obtained with it are reviewed. The applications reviewed here involve ion-atom and ion-molecule collisions, including electron-transfer processes. These exemplify typical results that generally agree well with experiment and provide new detailed insights into such phenomena. New results for an intramolecular electron-transfer process are reported here for the first time, too, using a simple but realistic model system. One can conclude that time-dependent treatments are able to attack a wide range of applications. For instance, they can be used, like time-independent ones, for separate electronic structure calculations, or for separate dynamics problems using precalculated PES's.

Commonly, for most small molecular problems, it has been logical to separate the electronic degrees of freedom from the nuclear ones by using the Born-Oppenheimer or the adiabatic approximation. Such a separation is optimal if one can efficiently obtain compact, preferably analytic, representations for the PES's at relevant nuclear geometries for all relevant stationary states. When this is so, this traditional approach offers a good alternative for many problems. However, even for systems of moderate complexity, the solutions of the electronic structure problem are only available as the result of a separate, rather demanding computational procedure. The necessary fitting of numerical representations of potential-energy surfaces to suitable analytical forms for use in dynamical problems also presents great challenges. The separate classical, semiclassical, or fully quantum-mechanical scattering treatments on even a single fitted surface are also extremely demanding. From the results obtained with the END theory implemented at the simplest possible level in the ENDyne code, one can conclude that in many cases consideration of the full problem as a single task constitutes a balanced, sufficiently accurate, and competitive approach for a variety of dynamical, and even spectroscopic, problems.

ACKNOWLEDGMENTS

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APPENDIX

1. Derivation in an orthonormal basis

In this section the ingredients of the dynamical equations are constructed for the representation in an orthonormal basis built with traveling atomic orbitals. The results for the representation in an orthonormal basis built with the nonfollowing AO's or with ordinary, following, AO's can be obtained easily by omitting all dependence on nuclear coordinates R and momenta P or by omitting all dependence on P, respectively. This implies that all derivatives with respect to omitted variables must be set equal to zero. In each formula the overlap and other quantities are shown with only the relevant parameters explicitly given.

a. Metric

From Eq. (3.7) the derivative with respect to the Thouless parameters is obtained as

$$\begin{aligned}\frac{\partial}{\partial z_{ph}}\ln\langle z'|z\rangle\Big|_{z'=z} &= \langle z|z\rangle^{-1}\frac{\partial}{\partial z_{ph}}\left[\sum_{g=1}^{N} M_{gh}\,\mathrm{Minor}(M)_{gh}\right]\Bigg|_{z'=z}\\ &= \langle z|z\rangle^{-1}\sum_{g=1}^{N}\frac{\partial M_{gh}}{\partial z_{ph}}\Bigg|_{z'=z}(M^{-1}|_{z'=z})_{hg}\langle z|z\rangle\\ &= \sum_{g=1}^{N} z^{*}_{pg}(I^{\bullet}+z^{\dagger}z)^{-1}_{hg}\\ &= [(I^{\bullet}+z^{\dagger}z)^{-1}z^{\dagger}]_{hp}\ . \end{aligned} \tag{A1}$$

In the first step the determinant is expanded in the column g with M denoting the matrix

$$M = I^{\bullet} + z'^{\dagger}z\ . \tag{A2}$$

The next step uses the expression for the inverse of a matrix in terms of its minors

$$(M^{-1})_{hg} = \frac{\mathrm{Minor}(M)_{gh}}{\det(M)} \tag{A3}$$

and the fact that none of the elements z_{ph} do occur in the minor gh because it does not contain column h of M. Similarly, one finds for the derivative, with respect to the complex conjugate of the Thouless parameters, in matrix form that

$$\frac{\partial}{\partial z^{*}}\ln\langle z'|z\rangle\Big|_{z'=z} = z(I^{\bullet}+z^{\dagger}z)^{-1}\ . \tag{A4}$$

Equation (3.29) shows that the general overlap for molecular orbitals built with TAO's is

$$\begin{aligned}&S_{\mathrm{el}}(z'^{*},R',P',z,R,P)\\ &\quad=\langle z'^{*},R',P'|z,R,P\rangle\\ &\quad=\det(\Delta^{\bullet}+\Delta^{>}z+z'^{\dagger}\Delta^{\vee}+z'^{\dagger}\Delta^{\circ}z)\ ,\end{aligned} \tag{A5}$$

from which the derivative with respect to the nuclear position can be evaluated. It is the purely imaginary quantity

$$\begin{aligned}&\nabla_{\mathbf{R}_k}\ln\langle z,R',P'|z,R,P\rangle\big|_{R'=R,P'=P}\\ &\quad=\mathrm{Tr}\left[(I^{\bullet}+z^{\dagger}z)^{-1}(I^{\bullet}\quad z^{\dagger})\nabla^{|\rangle}_{\mathbf{R}_k}\Delta\begin{bmatrix}I^{\bullet}\\ z\end{bmatrix}\right]\ ,\end{aligned} \tag{A6}$$

where the following property is used

$$\begin{aligned}\frac{\partial\ln\det(M)}{\partial x} &= \det(M)^{-1}\sum_{ij}\frac{\partial\det(M)}{\partial M_{ij}}\frac{\partial M_{ij}}{\partial x}\\ &= \sum_{ij}(M^{-1})_{ji}\frac{\partial M_{ij}}{\partial x}\\ &= \mathrm{Tr}M^{-1}\frac{\partial M}{\partial x}\ .\end{aligned} \tag{A7}$$

One should note that the derivatives of the overlap matrix in Eq. (A6) are to be taken with respect to the R dependence of one side only. The derivatives with respect to the nuclear momenta are given by an identical expression, but with the gradients with respect to P. They are not shown in the following unless they are really different.

This derivative gives the expectation value of the electronic momentum, provided all dependence of the atomic orbitals on the electronic coordinates is of the form $\mathbf{r}-\mathbf{R}_k$ for some center k. In that case,

$$\mathbf{p}=\sum_{n=1}^{N}\langle z,R,P|-i\nabla_{\mathbf{r}_n}|z,R,P\rangle/\langle z,R,P|z,R,P\rangle$$
$$=i\sum_{k=1}^{N_{\text{nuc}}}\nabla_{\mathbf{R}_k}\ln\langle z,R',P|z,R,P\rangle|_{R'=R}\ . \tag{A8}$$

For the second derivatives of the overlap, the derivatives of the inverse of M are needed. From the relation

$$XX^{-1}=I \tag{A9}$$

for any matrix X depending on a variable x, it follows that

$$\frac{\partial X^{-1}}{\partial x}=-X^{-1}\frac{\partial X}{\partial x}X^{-1}\ . \tag{A10}$$

Therefore the derivatives of the inverse of M are

$$\frac{\partial}{\partial z^*_{ph}}[(I^{\bullet}+z^{\dagger}z)^{-1}]_{mn}=-[(I^{\bullet}+z^{\dagger}z)^{-1}]_{mh}[z(I^{\bullet}+z^{\dagger}z)^{-1}]_{pn}\ . \tag{A11}$$

The second derivatives of the overlap with respect to the Thouless parameters are then given by

$$\frac{\partial^2\ln\langle z|z\rangle}{\partial z_{qg}\partial z_{ph}}=\sum_{i=1}^{N}\frac{\partial}{\partial z_{qg}}[(I^{\bullet}+z^{\dagger}z)^{-1}]_{hi}(z^{\dagger})_{ip}$$
$$=-[(I^{\bullet}+z^{\dagger}z)^{-1}z^{\dagger}]_{hq}[(I^{\bullet}+z^{\dagger}z)^{-1}z^{\dagger}]_{gp} \tag{A12}$$

and

$$\frac{\partial^2\ln\langle z|z\rangle}{\partial z^*_{qg}\partial z_{ph}}=\sum_{i=1}^{N}\frac{\partial}{\partial z^*_{qg}}[(I^{\bullet}+z^{\dagger}z)^{-1}]_{hi}(z^{\dagger})_{ip}+[(I^{\bullet}+z^{\dagger}z)^{-1}]_{hg}\delta_{qp}$$
$$=[(I^{\bullet}+z^{\dagger}z)^{-1}]_{hg}[I^{\circ}-z(I^{\bullet}+z^{\dagger}z)^{-1}z^{\dagger}]_{qp}$$
$$=[(I^{\bullet}+z^{\dagger}z)^{-1}]_{hg}[(I^{\circ}+zz^{\dagger})^{-1}]_{qp}\ , \tag{A13}$$

where the bottom-right block in Eq. (2.28) is used in the last step. The mixed second derivatives with respect to nuclear positions (momenta), Eq. (3.37), involve the ket-gradient of the orbital overlap matrix Δ

$$\frac{\partial}{\partial z'^*}\nabla_{\mathbf{R}_k}\ln\langle z',R'|z,R\rangle|_{z'=z,R'=R}=(0\quad I^{\circ})\nabla^{|\rangle}_{\mathbf{R}_k}\Delta\begin{bmatrix}I^{\bullet}\\ z\end{bmatrix}(I^{\bullet}+z^{\dagger}z)^{-1}-z(I^{\bullet}+z^{\dagger}z)^{-1}(I^{\bullet}\quad z^{\dagger})\nabla^{|\rangle}_{\mathbf{R}_k}\Delta\begin{bmatrix}I^{\bullet}\\ z\end{bmatrix}(I^{\bullet}+z^{\dagger}z)^{-1}$$
$$=(I^{\circ}+zz^{\dagger})^{-1}(-z\quad I^{\circ})\nabla^{|\rangle}_{\mathbf{R}_k}\Delta\begin{bmatrix}I^{\bullet}\\ z\end{bmatrix}(I^{\bullet}+z^{\dagger}z)^{-1}=C_{\mathbf{R}_k}\ , \tag{A14}$$

where the bottom-left block in Eq. (2.28) is used. The second derivatives with respect to the nuclear positions (momenta), Eq. (3.38), are

$$\nabla_{\mathbf{R}'_k}\nabla_{\mathbf{R}_l}\ln\langle z',R'|z,R\rangle|_{z'=z,R'=R}=\mathrm{Tr}\left[(I^{\bullet}+z^{\dagger}z)^{-1}(I^{\bullet}\quad z^{\dagger})\nabla^{\langle|}_{\mathbf{R}_k}\nabla^{|\rangle}_{\mathbf{R}_l}\Delta\begin{bmatrix}I^{\bullet}\\ z\end{bmatrix}\right.$$
$$\left.-(I^{\bullet}+z^{\dagger}z)^{-1}(I^{\bullet}\quad z^{\dagger})\nabla^{\langle|}_{\mathbf{R}_k}\Delta\begin{bmatrix}I^{\bullet}\\ z\end{bmatrix}(I^{\bullet}+z^{\dagger}z)^{-1}(I^{\bullet}\quad z^{\dagger})\nabla^{|\rangle}_{\mathbf{R}_l}\Delta|\begin{bmatrix}I^{\bullet}\\ z\end{bmatrix}\right]\ , \tag{A15}$$

which is a Hermitian matrix.

b. Density matrix

The one-matrix, Eq. (3.8), has the block form, Eq. (3.9). For the occupied block, the following equation holds,

$$\begin{aligned}\Gamma^{\bullet}_{gh}&=\langle z|z\rangle^{-1}\langle\mathrm{vac}|\left[b^{\bullet}_{h}\prod_{l=1}^{N}\left[b^{\bullet\dagger}_{l}+\sum_{m=N+1}^{K}b^{\circ\dagger}_{m}z_{ml}\right]\right]^{\dagger}b^{\bullet}_{g}\prod_{k=1}^{N}\left[b^{\bullet\dagger}_{k}+\sum_{m=N+1}^{K}b^{\circ\dagger}_{m}z_{mk}\right]|\mathrm{vac}\rangle\\&=\langle z|z\rangle^{-1}(-)^{h+g}\det\left\{(\delta_{ij}+\sum_{m=N+1}^{K}z^{*}_{mi}z_{mj})_{i\neq h,j\neq g}\right\}_{ij}\\&=\det(\boldsymbol{M})^{-1}\mathrm{Minor}(\boldsymbol{M})_{hg}\\&=[(\boldsymbol{I}^{\bullet}+z^{\dagger}z)^{-1}]_{gh}\ .\end{aligned}\tag{A16}$$

The unoccupied block has the form

$$\begin{aligned}\Gamma^{\circ}_{qp}=\langle z|z\rangle^{-1}\langle\mathrm{vac}|&\left[\left[z_{p1}-\left[b^{\bullet\dagger}_{1}+\sum_{m=N+1}^{K}b^{\circ\dagger}_{m}z_{m1}\right]b^{\circ}_{p}\right]\prod_{l=2}^{N}\left[b^{\bullet}_{l}+\sum_{m=N+1}^{K}b^{\circ}_{m}z^{*}_{ml}\right]\right]^{\dagger}\\&\times\left[z_{q1}-\left[b^{\bullet\dagger}_{1}+\sum_{m=N+1}^{K}b^{\circ\dagger}_{m}z_{m1}\right]b^{\circ}_{q}\right]\prod_{k=2}^{N}\left[b^{\bullet\dagger}_{k}+\sum_{m=N+1}^{K}b^{\circ\dagger}_{m}z_{mk}\right]|\mathrm{vac}\rangle\ .\end{aligned}\tag{A17}$$

Moving the annihilators further through yields

$$\begin{aligned}\Gamma^{\circ}_{qp}&=\langle z|z\rangle^{-1}\sum_{l=1}^{N}\sum_{k=1}^{N}z^{*}_{pl}z_{qk}(-)^{k+l}\det\left\{\left[\delta_{ij}+\sum_{m=1}^{K}z^{*}_{mi}z_{mj}\right]_{i\neq l,j\neq k}\right\}_{ij}\\&=\det(\boldsymbol{M})^{-1}\sum_{k=1}^{N}z_{qk}\mathrm{Minor}(\boldsymbol{M})_{lk}z^{*}_{pl}\end{aligned}\tag{A18}$$

so that

$$\Gamma^{\circ}_{qp}=[z(\boldsymbol{I}^{\bullet}+z^{\dagger}z)^{-1}z^{\dagger}]_{qp}\ .\tag{A19}$$

The off-diagonal block is obtained with the help of the first derivatives of the logarithm of the overlap kernel from

$$\begin{aligned}\Gamma^{>}_{hp}&=\langle z|z\rangle^{-1}\langle z|b^{\circ\dagger}_{p}b^{\bullet}_{h}|z\rangle\\&=\frac{\partial}{\partial z_{ph}}\ln\langle z|z\rangle\\&=[(\boldsymbol{I}^{\bullet}+z^{\dagger}z)^{-1}z^{\dagger}]_{hp}\ .\end{aligned}\tag{A20}$$

Therefore the full one-matrix is given by

$$\Gamma(z^{*},z)=\begin{bmatrix}\boldsymbol{I}^{\bullet}\\ z\end{bmatrix}(\boldsymbol{I}^{\bullet}+z^{\dagger}z)^{-1}(\boldsymbol{I}^{\bullet}\quad z^{\dagger})\ .\tag{A21}$$

Note that this is the projector onto the nonorthogonal occupied orbitals (Löwdin, 1955).

The derivatives of the energy can be written much more elegantly in terms of the derivatives of the one-particle density matrix. Equation (A11) gives with the bottom-left block in Eq. (2.28) the first derivative with respect to z^{*},

$$\frac{\partial\Gamma_{ij}}{\partial z^{*}_{ph}}=\left[\begin{bmatrix}\boldsymbol{I}^{\bullet}\\ z\end{bmatrix}(\boldsymbol{I}^{\bullet}+z^{\dagger}z)^{-1}\right]_{ih}[(\boldsymbol{I}^{\circ}+zz^{\dagger})^{-1}(-z\quad\boldsymbol{I}^{\circ})]_{pj}\ ,\tag{A22}$$

and, by taking the adjoint, the first derivative with respect to z follows. Because the basis is orthonormal at each geometry, there are no total gradients with respect to the nuclear positions and momenta even if the molecular orbitals change and the bra gradients and ket gradients are nonzero.

The second derivative with respect to z^{*} and z then follows as

$$\frac{\partial^2\Gamma_{ij}}{\partial z^*_{ph}\partial z_{qg}}=\left[\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}(I^{\bullet}+z^{\dagger}z)^{-1}\right]_{ih}\{[(I^{\circ}+zz^{\dagger})^{-1}]_{pq}[(-I^{\bullet}\quad 0)]_{gj}-[(I^{\circ}+zz^{\dagger})^{-1}]_{pq}[z^{\dagger}(I^{\circ}+zz^{\dagger})^{-1}(-z\quad I^{\circ})]_{gj}\}$$
$$+\left\{-\left[\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}(I^{\bullet}+z^{\dagger}z)^{-1}z^{\dagger}\right]_{iq}[(I^{\bullet}+z^{\dagger}z)^{-1}]_{gh}+\begin{bmatrix} 0 \\ I^{\circ} \end{bmatrix}_{iq}[(I^{\bullet}+z^{\dagger}z)^{-1}]_{gh}\right\}[(I^{\circ}+zz^{\dagger})^{-1}(-z\quad I^{\circ})]_{pj}\;. \tag{A23}$$

This equation can be simplified by manipulating the 1×2 block matrices in the first two terms using the bottom-left block in Eq. (2.28) to find

$$[-I^{\bullet}+z^{\dagger}(I^{\circ}+zz^{\dagger})^{-1}z\;-z^{\dagger}(I^{\circ}+zz^{\dagger})^{-1}]=-(I^{\bullet}+z^{\dagger}z)^{-1}(I^{\bullet}\quad z^{\dagger})\;. \tag{A24}$$

Similarly, the 2×1 block matrices in the last two terms can be taken together, i.e.,

$$\begin{bmatrix} -(I^{\bullet}+z^{\dagger}z)^{-1}z^{\dagger} \\ I^{\circ}-z(I^{\bullet}+z^{\dagger}z)^{-1}z^{\dagger} \end{bmatrix}=\begin{bmatrix} -z^{\dagger}(I^{\circ}+zz^{\dagger})^{-1} \\ (I^{\circ}+zz^{\dagger})^{-1} \end{bmatrix}=\begin{bmatrix} -z^{\dagger} \\ I^{\circ} \end{bmatrix}(I^{\circ}+zz^{\dagger})^{-1}\;. \tag{A25}$$

Therefore

$$\frac{\partial^2\Gamma_{ij}}{\partial z^*_{ph}\partial z_{qg}}=-\left[\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}(I^{\bullet}+z^{\dagger}z)^{-1}\right]_{ih}[(I^{\circ}+zz^{\dagger})^{-1}]_{pq}[(I^{\bullet}+z^{\dagger}z)^{-1}(I^{\bullet}\quad z^{\dagger})]_{gj}$$
$$+\left[\begin{bmatrix} -z^{\dagger} \\ I^{\circ} \end{bmatrix}(I^{\circ}+zz^{\dagger})^{-1}\right]_{iq}[(I^{\bullet}+z^{\dagger}z)^{-1}]_{gh}[(I^{\circ}+zz^{\dagger})^{-1}(-z\quad I^{\circ})]_{pj}\;. \tag{A26}$$

Note that this equation goes over into its complex conjugate when p,h,i are interchanged with q,g,j, respectively. For the second derivative with respect to z^*, one gets, again using Eq. (2.28),

$$\frac{\partial^2\Gamma_{ij}}{\partial z^*_{ph}\partial z^*_{qg}}=-\left[\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}(I^{\bullet}+z^{\dagger}z)^{-1}\right]_{ih}[z(I^{\bullet}+z^{\dagger}z)^{-1}]_{pg}[(I^{\circ}+zz^{\dagger})^{-1}(-z\quad I^{\circ})]_{qj}$$
$$-\left[\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}(I^{\bullet}+z^{\dagger}z)^{-1}\right]_{ig}[z(I^{\bullet}+z^{\dagger}z)^{-1}]_{qh}[(I^{\circ}+zz^{\dagger})^{-1}(-z\quad I^{\circ})]_{pj}\;. \tag{A27}$$

This equation is invariant with respect to interchange of p,h and q,g.

c. Energy

With Eqs. (A21) and (3.10) for the densities, the total energy of the molecular state is given by Eq. (3.12). Using the derivatives, Eq. (A22), of the one-density, we obtain the derivatives with respect to z^* of the one-electron energy,

$$\frac{\partial E^{(1)}(z^*,z,R,P)}{\partial z^*_{ph}}=\left[(I^{\circ}+zz^{\dagger})^{-1}(-z\quad I^{\circ})h\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}(I^{\bullet}+z^{\dagger}z)^{-1}\right]_{ph}\;. \tag{A28}$$

Applying the same calculation to the double trace and using symmetries (3.5) and (3.6) of the antisymmetrized two-electron integrals, we obtain the derivatives with respect to z^* of the two-electron term. Combined with the one-electron term, and since the zero-electron term (3.11) does not depend on z, the derivative of the total energy with respect to the Thouless parameters is given as

$$\frac{\partial E(z^*,z)}{\partial z^*_{ph}}=\left[(I^{\circ}+zz^{\dagger})^{-1}(-z\quad I^{\circ})F\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}(I^{\bullet}+z^{\dagger}z)^{-1}\right]_{ph}\;, \tag{A29}$$

with the Fock operator (3.23).

The derivatives with respect to the nuclear positions R and momenta P are obtained by taking Eq. (3.12) with the one- and two-electron integrals h and V replaced by the corresponding derivative-integrals. Because the full gradient is considered, as opposed to the bra- or ket-gradient, there are no contributions from the orthonormal orbital overlap matrix. Explicitly, one gets

$$\nabla_{\mathbf{R}_k} E(z^*,z,R,P) = -\sum_{\substack{l=1\\ l\neq k}}^{N_{\mathrm{at}}} \frac{Z_k Z_l e^2(\mathbf{R}_k-\mathbf{R}_l)}{|\mathbf{R}_k-\mathbf{R}_l|^3} + \mathrm{Tr}(\nabla_{\mathbf{R}_k} h\Gamma) + \tfrac{1}{2}\mathrm{Tr}[\mathrm{Tr}(\nabla_{\mathbf{R}_k} V_{ab;ab}\Gamma)_a\Gamma]_b \, . \tag{A30}$$

The derivatives with respect to nuclear momenta are

$$\nabla_{\mathbf{P}_k} E(z^*,z,R,P) = \frac{\mathbf{P}_k}{M_k} + \mathrm{Tr}(\nabla_{\mathbf{P}_k} h\Gamma) + \tfrac{1}{2}\mathrm{Tr}[\mathrm{Tr}(\nabla_{\mathbf{P}_k} V_{ab;ab}\Gamma)_a\Gamma]_b \, , \tag{A31}$$

assuming TAO's are used for the electrons. The terms after the first are not present when ordinary AO's, without ETF's, are used.

With the derivatives of the one-particle density, the second derivatives of the energy defined in Eq. (3.63) become simple. The second derivatives with respect to the Thouless parameters are (A)

$$\frac{\partial^2 E(z^*,z)}{\partial z^*_{ph}\partial z_{qg}} = \mathrm{Tr}\left[[h+\mathrm{Tr}(V_{ab;ab}\Gamma)_a]\frac{\partial^2\Gamma}{\partial z^*_{ph}\partial z_{qg}}\right]_b + \mathrm{Tr}\left[\mathrm{Tr}\left[V_{ab;ab}\frac{\partial\Gamma}{\partial z^*_{ph}}\right]_a \frac{\partial\Gamma}{\partial z_{qg}}\right]_b \tag{A32}$$

and (B)

$$\frac{\partial^2 E(z^*,z)}{\partial z^*_{ph}\partial z^*_{qg}} = \mathrm{Tr}\left[[h+\mathrm{Tr}(V_{ab;ab}\Gamma)_a]\frac{\partial^2\Gamma}{\partial z^*_{ph}\partial z^*_{qg}}\right]_b + \mathrm{Tr}\left[\mathrm{Tr}\left[V_{ab;ab}\frac{\partial\Gamma}{\partial z^*_{ph}}\right]_a \frac{\partial\Gamma}{\partial z^*_{qg}}\right]_b \, . \tag{A33}$$

Note that as a consequence of the symmetries of the derivatives of Γ, the familiar properties of the random-phase-approximation matrices are recognized; i.e., (A) is Hermitian and (B) is symmetric when p,h are replaced with q,g, respectively. The mixed derivative involving nuclear positions is (F)

$$\frac{\partial}{\partial z^*_{ph}}\nabla_{\mathbf{R}_k} E(z^*,z,R,P) = \mathrm{Tr}\left[[\nabla_{\mathbf{R}_k} h+\mathrm{Tr}(\nabla_{\mathbf{R}_k} V_{ab;ab}\Gamma)_a]\frac{\partial\Gamma}{\partial z^*_{ph}}\right] . \tag{A34}$$

The matrix G is the same with the R gradient replaced by a P gradient. The second derivatives with respect to nuclear positions are given by (I)

$$\begin{aligned}\nabla_{\mathbf{R}_k}\nabla_{\mathbf{R}_l} E(z^*,z,R,P) = {}& -\frac{Z_k Z_l e^2[3(\mathbf{R}_k-\mathbf{R}_l)(\mathbf{R}_k-\mathbf{R}_l)-|\mathbf{R}_k-\mathbf{R}_l|^2]}{|\mathbf{R}_k-\mathbf{R}_l|^5}\\ &+\delta_{kl}\sum_{\substack{n=1\\ n\neq l}}^{N_{\mathrm{at}}}\frac{Z_n Z_l e^2[3(\mathbf{R}_n-\mathbf{R}_l)(\mathbf{R}_n-\mathbf{R}_l)-|\mathbf{R}_n-\mathbf{R}_l|^2]}{|\mathbf{R}_n-\mathbf{R}_l|^5}\\ &+\mathrm{Tr}\{[\nabla_{\mathbf{R}_k}\nabla_{\mathbf{R}_l} h+\tfrac{1}{2}\mathrm{Tr}(\nabla_{\mathbf{R}_k}\nabla_{\mathbf{R}_l} V_{ab;ab}\Gamma)_a]\Gamma\} \, .\end{aligned} \tag{A35}$$

The second derivatives with respect to the nuclear momenta are just the kinetic-energy terms (J) plus terms coming from ETF's,

$$\nabla_{\mathbf{P}_k}\nabla_{\mathbf{P}_l} E(z^*,z,R,P) = \frac{1}{M_k}\delta_{kl} + \mathrm{Tr}\{[\nabla_{\mathbf{P}_k}\nabla_{\mathbf{P}_l} h+\frac{1}{2}\mathrm{Tr}(\nabla_{\mathbf{P}_k}\nabla_{\mathbf{P}_l} V_{ab;ab}\Gamma)_a]\Gamma\} \, ; \tag{A36}$$

and the mixed derivatives are (K)

$$\nabla_{\mathbf{R}_k}\nabla_{\mathbf{P}_l} E(z^*,z,R,P) = \mathrm{Tr}\{[\nabla_{\mathbf{R}_k}\nabla_{\mathbf{P}_l} h+\tfrac{1}{2}\mathrm{Tr}(\nabla_{\mathbf{R}_k}\nabla_{\mathbf{P}_l} V_{ab;ab}\Gamma)_a]\Gamma\} \, . \tag{A37}$$

2. Derivation in the atomic-orbital basis

In this section the components of the evolution equations are derived for the representation in the nonorthogonal traveling atomic-orbital basis. The results for the representation in the customary, i.e., following, atomic-orbital basis can be obtained easily by omitting all dependence on nuclear momenta P. This implies that all derivatives with respect to omitted momenta must be set equal to zero. For didactic purposes, the transformation is applied for some quantities, while for others the expressions are completely rederived with the new parametrization.

a. Definition of parameters

In this section, the transformation, Eq. (3.46) of Sec. III.B.1, from Thouless parameters z in an orthonormal molecular basis to Thouless parameters z in the atomic basis is constructed. One can always mix occupied orbitals among themselves and transform unoccupied orbitals without changing the state. This freedom can be used to keep the form of the parametrization the same. Given (1) the transformation W (2.19) to an orthonormal reference basis and (2) the parameters z for the determinantal state with respect to that reference basis, one can suitably define (1) a set of parameters $\tilde{z}$ for the determinantal state with respect to the atomic basis of the same form as z and (2) an auxiliary transformation matrix U, such that the same state is defined in the atomic basis. One needs to solve

$$\begin{aligned} &\begin{bmatrix} W^{\bullet} & W^{>} \\ W^{\vee} & W^{\circ} \end{bmatrix} \begin{bmatrix} I^{\bullet} & 0 \\ z & I^{\circ} \end{bmatrix} = \begin{bmatrix} I^{\bullet} & 0 \\ \tilde{z} & I^{\circ} \end{bmatrix} \begin{bmatrix} U^{\bullet} & U^{>} \\ U^{\vee} & U^{\circ} \end{bmatrix} , \\ &\begin{bmatrix} W^{\bullet}+W^{>}z & W^{>} \\ W^{\vee}+W^{\circ}z & W^{\circ} \end{bmatrix} = \begin{bmatrix} U^{\bullet} & U^{>} \\ \tilde{z}U^{\bullet}+U^{\vee} & \tilde{z}U'+U^{\circ} \end{bmatrix} \end{aligned} \tag{A38}$$

for U and $\tilde{z}$. One solution that satisfies the above criteria is easily found to be

$$\begin{aligned} &U^{>}=W^{>} , \\ &U^{\bullet}=W^{\bullet}+W^{>}z , \\ &U^{\vee}=W^{\vee} , \\ &\tilde{z}=W^{\circ}z(W^{\bullet}+W^{>}z)^{-1} , \\ &U^{\circ}=W^{\circ}-W^{\circ}z(W^{\bullet}+W^{>}z)^{-1}U^{>} . \end{aligned} \tag{A39}$$

Straightforwardly, the inverse follows,

$$z=(W^{\circ}-\tilde{z}W^{>})^{-1}\tilde{z}W^{\bullet} . \tag{A40}$$

Note that the first symplectic transformation, to TAO's, is linear in z, while this second symplectic transformation is a conformal mapping in z.

The matrix U will have no effect on the determinantal state if it mixes occupied orbitals among themselves, or transforms unoccupied orbitals, while it will have an effect if it mixes unoccupied orbitals into the occupied orbitals. Hence one must require $U^{\vee}=W^{\vee}=0$. This means that the reference orthonormal basis that yields the desired parametrization is given by

$$\begin{aligned} &\psi^{\bullet}=\phi^{\bullet}W^{\bullet} , \\ &\psi^{\circ}=\phi^{\bullet}W^{>}+\phi^{\circ}W^{\circ} . \end{aligned} \tag{A41}$$

It is constructed by first orthonormalizing the occupied atomic orbitals among themselves, and then orthonormalizing the unoccupied atomic orbitals to the occupied space and among themselves. This has the effect that the occupied space is the same space whether defined in the nonorthogonal atomic or in this orthonormal molecular basis.

The determinantal state, Eq. (2.21), is thus equal to

$$\begin{aligned} |\Psi_z\rangle=|\Phi_{\tilde{z}}\rangle &=\alpha \prod_{h=1}^{N} \left[b_h^{\bullet\dagger}+\sum_{p=N+1}^{K} b_p^{\circ\dagger}z_{ph} \right] |\text{vac}\rangle \\ &=\tilde{\alpha} \prod_{h=1}^{N} \left[a_h^{\bullet\dagger}+\sum_{p=N+1}^{K} a_p^{\circ\dagger}\tilde{z}_{ph} \right] |\text{vac}\rangle \\ &=\tilde{\alpha} \prod_{h=1}^{N} (\tilde{c}_h)^{\bullet\dagger}|\text{vac}\rangle \\ &=\tilde{\alpha}|\tilde{z}\rangle , \end{aligned} \tag{A42}$$

where the constants α are different because of the extra factor U arising from the transformation (A38) to atomic parameters. As before, one considers the unnormalized state

$$\begin{aligned} |\tilde{z}\rangle &= \prod_{h=1}^{N} (\tilde{c}_h)^{\bullet\dagger}|\text{vac}\rangle \\ &= \prod_{h=1}^{N} \left[a_h^{\bullet\dagger}+\sum_{p=N+1}^{K} a_p^{\circ\dagger}\tilde{z}_{ph} \right] |\text{vac}\rangle . \end{aligned} \tag{A43}$$

The normalization (2.4) leads to some valuable relations for the blocks of W if $W^{\vee}=0$. Now consider

$$\begin{aligned} &\begin{bmatrix} W^{\bullet\dagger} & 0 \\ W^{>\dagger} & W^{\circ\dagger} \end{bmatrix} \begin{bmatrix} \Delta^{\bullet} & \Delta^{>} \\ \Delta^{\vee} & \Delta^{\circ} \end{bmatrix} \begin{bmatrix} W^{\bullet} & W^{>} \\ 0 & W^{\circ} \end{bmatrix} \\ &\quad = \begin{bmatrix} I^{\bullet} & 0 \\ 0 & I^{\circ} \end{bmatrix} \\ &\quad = \begin{bmatrix} W^{\bullet\dagger} & 0 \\ W^{>\dagger} & W^{\circ\dagger} \end{bmatrix} \begin{bmatrix} \Delta^{\bullet}W^{\bullet} & \Delta^{\bullet}W^{>}+\Delta^{>}W^{\circ} \\ \Delta^{\vee}W^{\bullet} & \Delta^{\vee}W^{>}+\Delta^{\circ}W^{\circ} \end{bmatrix} \\ &\quad = \begin{bmatrix} W^{\bullet\dagger}\Delta^{\bullet}W^{\bullet} & W^{\bullet\dagger}\Delta^{\bullet}W^{>}+W^{\bullet\dagger}\Delta^{>}W^{\circ} \\ W^{>\dagger}\Delta^{\bullet}W^{\bullet}+W^{\circ\dagger}\Delta^{\vee}W^{\bullet} & W^{>\dagger}\Delta^{\bullet}W^{>}+W^{>\dagger}\Delta^{>}W^{\circ}+W^{\circ\dagger}\Delta^{\vee}W^{>}+W^{\circ\dagger}\Delta^{\circ}W^{\circ} \end{bmatrix} \end{aligned} \tag{A44}$$

and note that it follows, from the upper diagonal, that

$$W^{\bullet\dagger}\Delta^{\bullet}W^{\bullet}=I^{\bullet} \tag{A45}$$

and, from the upper off-diagonal, that

$$W^{>}=-\Delta^{\bullet -1}\Delta^{>}W^{\circ}\tag{A46}$$

and, finally, from the lower diagonal, that

$$\begin{aligned}W^{\circ\dagger}\Delta^{\circ}W^{\circ}+W^{\circ\dagger}\Delta^{\vee}W^{>}+W^{>\dagger}\Delta^{>}W^{\circ}+W^{>\dagger}\Delta^{\bullet}W^{>}&=W^{\circ\dagger}\Delta^{\circ}W^{\circ}-W^{\circ\dagger}\Delta^{\vee}\Delta^{\bullet -1}\Delta^{>}W^{\circ}\\&=W^{\circ\dagger}(\Delta^{\circ}-\Delta^{\vee}\Delta^{\bullet -1}\Delta^{>})W^{\circ}\\&=I^{\circ}\ .\end{aligned}\tag{A47}$$

From (A45)

$$\Delta^{\bullet}=W^{\bullet\dagger -1}W^{\bullet -1}\tag{A48}$$

and (A47), it follows that

$$\Delta^{\circ}-\Delta^{\vee}\Delta^{\bullet -1}\Delta^{>}=W^{\circ\dagger -1}W^{\circ -1}\ .\tag{A49}$$

One explicit possibility for W that satisfies the requirements is

$$W=\begin{bmatrix}\Delta^{\bullet -1/2} & -\Delta^{\bullet -1}\Delta^{>}(\Delta^{\circ}-\Delta^{\vee}\Delta^{\bullet -1}\Delta^{>})^{-1/2}\\ 0 & (\Delta^{\circ}-\Delta^{\vee}\Delta^{\bullet -1}\Delta^{>})^{-1/2}\end{bmatrix}\ .\tag{A50}$$

It is also possible to obtain some equations for the blocks of the inverse $X=W^{-1}$, which are important for the transformations back and forth between the atomic and molecular basis. From

$$\begin{aligned}\begin{bmatrix}W^{\bullet} & W^{>}\\ 0 & W^{\circ}\end{bmatrix}\begin{bmatrix}X^{\bullet} & X^{>}\\ X^{\vee} & X^{\circ}\end{bmatrix}&=\begin{bmatrix}W^{\bullet}X^{\bullet}+W^{>}X^{\vee} & W^{\bullet}X^{>}+W^{>}X^{\circ}\\ W^{\circ}X^{\vee} & W^{\circ}X^{\circ}\end{bmatrix}\\&=\begin{bmatrix}I^{\bullet} & 0\\ 0 & I^{\circ}\end{bmatrix}\end{aligned}\tag{A51}$$

and

$$\begin{aligned}\begin{bmatrix}X^{\bullet} & X^{>}\\ X^{\vee} & X^{\circ}\end{bmatrix}\begin{bmatrix}W^{\bullet} & W^{>}\\ 0 & W^{\circ}\end{bmatrix}&=\begin{bmatrix}X^{\bullet}W^{\bullet} & X^{\bullet}W^{>}+X^{>}W^{\circ}\\ X^{\vee}W^{\bullet} & X^{\vee}W^{>}+X^{\circ}W^{\circ}\end{bmatrix}\\&=\begin{bmatrix}I^{\bullet} & 0\\ 0 & I^{\circ}\end{bmatrix}\ ,\end{aligned}\tag{A52}$$

one gets

$$W^{-1}=X=\begin{bmatrix}W^{\bullet -1} & -W^{\bullet -1}W^{>}W^{\circ -1}\\ 0 & W^{\circ -1}\end{bmatrix}\ .\tag{A53}$$

b. Dynamic orbitals

In the case of an orthonormal basis, Eq. (2.28) can be obtained by direct computation. In the atomic basis, the situation is different. One is then looking for a $(K-N)\times N$ matrix v, defining a set of virtual orbitals, such that the occupied and unoccupied spaces are orthogonal

$$\begin{aligned}\begin{bmatrix}I^{\bullet} & z^{\dagger}\\ v & I^{\circ}\end{bmatrix}\Delta\begin{bmatrix}I^{\bullet} & v^{\dagger}\\ z & I^{\circ}\end{bmatrix}&=\begin{bmatrix}\Delta^{\bullet}+z^{\dagger}\Delta^{\vee}+\Delta^{>}z+z^{\dagger}\Delta^{\circ}z & \Delta^{\bullet}v^{\dagger}+\Delta^{>}+z^{\dagger}\Delta^{\vee}v^{\dagger}+z^{\dagger}\Delta^{\circ}\\ v\Delta^{\bullet}+v\Delta^{>}z+\Delta^{\vee}+\Delta^{\circ}z & \Delta^{\circ}+v\Delta^{>}+\Delta^{\vee}v^{\dagger}+v\Delta^{\bullet}v^{\dagger}\end{bmatrix}\\&=\begin{bmatrix}\Delta^{\bullet}+z^{\dagger}\Delta^{\vee}+\Delta^{>}z+z^{\dagger}\Delta^{\circ}z & 0\\ 0 & \Delta^{\circ}+v\Delta^{>}+\Delta^{\vee}v^{\dagger}+v\Delta^{\bullet}v^{\dagger}\end{bmatrix}\ .\end{aligned}\tag{A54}$$

This requires the off-diagonal blocks to be zero,

$$v\Delta^{\bullet}+v\Delta^{>}z=-\Delta^{\vee}-\Delta^{\circ}z\ ,\tag{A55}$$

and hence

$$v=-(\Delta^{\vee}+\Delta^{\circ}z)(\Delta^{\bullet}+\Delta^{>}z)^{-1}\ .\tag{A56}$$

Now one can look at the equation for the projectors, (2.27), to derive the generalization of the relations (2.28) and note that matrices of the projection operators are considered. The matrices

$$\Lambda^{\bullet}(z)=\Delta^{\bullet}+z^{\dagger}\Delta^{\vee}+\Delta^{>}z+z^{\dagger}\Delta^{\circ}z \tag{A57}$$

and

$$\Lambda^{\circ}(v)=\Delta^{\circ}+v\Delta^{>}+\Delta^{\vee}v^{\dagger}+v\Delta^{\bullet}v^{\dagger} \tag{A58}$$

naturally occur in many expressions. The generalization of Eq. (2.28) is

$$\begin{aligned}
\Delta\Delta^{-1}\Delta-&\begin{bmatrix}\Delta^{\bullet}+\Delta^{>}z\\ \Delta^{\vee}+\Delta^{\circ}z\end{bmatrix}\Lambda^{\bullet}(z)^{-1}(\Delta^{\bullet}+z^{\dagger}\Delta^{\vee}\quad \Delta^{>}+z^{\dagger}\Delta^{\circ})\\
&=\begin{bmatrix}\Delta^{\bullet}-(\Delta^{\bullet}+\Delta^{>}z)\Lambda^{\bullet}(z)^{-1}(\Delta^{\bullet}+z^{\dagger}\Delta^{\vee}) & \Delta^{>}-(\Delta^{\bullet}+\Delta^{>}z)\Lambda^{\bullet}(z)^{-1}(\Delta^{>}+z^{\dagger}\Delta^{\circ})\\ \Delta^{>\dagger}-(\Delta^{\vee}+\Delta^{\circ}z)\Lambda^{\bullet}(z)^{-1}(\Delta^{\bullet}+z^{\dagger}\Delta^{\vee}) & \Delta^{\circ}-(\Delta^{\vee}+\Delta^{\circ}z)\Lambda^{\bullet}(z)^{-1}(\Delta^{>}+z^{\dagger}\Delta^{\circ})\end{bmatrix}\\
&=\begin{bmatrix}\Delta^{\bullet}v^{\dagger}+\Delta^{>}\\ \Delta^{\vee}v^{\dagger}+\Delta^{\circ}\end{bmatrix}\Lambda^{\circ}(v)^{-1}(v\Delta^{\bullet}+\Delta^{\vee}\quad v\Delta^{>}+\Delta^{\circ})\\
&=\begin{bmatrix}(\Delta^{\bullet}v^{\dagger}+\Delta^{>})\Lambda^{\circ}(v)^{-1}(v\Delta^{\bullet}+\Delta^{\vee}) & (\Delta^{\bullet}v^{\dagger}+\Delta^{>})\Lambda^{\circ}(v)^{-1}(v\Delta^{>}+\Delta^{\circ})\\ (\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(v\Delta^{\bullet}+\Delta^{\vee}) & (\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(v\Delta^{>}+\Delta^{\circ})\end{bmatrix}\ .
\end{aligned} \tag{A59}$$

This expression makes it possible to obtain exactly the same form of the evolution equations in the atomic basis as in the orthonormal basis.

Using definition (A56), the derivatives of the virtual orbital coefficients v with respect to the Thouless parameters z become

$$\begin{aligned}
\frac{\partial v_{qg}}{\partial z_{ph}}&=-\Delta^{\circ}_{qp}[(\Delta^{\bullet}+\Delta^{>}z)^{-1}]_{hg}+[(\Delta^{\vee}+\Delta^{\circ}z)(\Delta^{\bullet}+\Delta^{>}z)^{-1}\Delta^{>}]_{qp}[(\Delta^{\bullet}+\Delta^{>}z)^{-1}]_{hg}\\
&=-(\Delta^{\circ}+v\Delta^{>})_{qp}[(\Delta^{\bullet}+\Delta^{>}z)^{-1}]_{hg}\ .
\end{aligned} \tag{A60}$$

c. Metric

The derivatives of the logarithm of the overlap equation (3.29) have to be computed. Repeating the calculations in Eqs. (A1)–(A6), one obtains

$$\begin{aligned}
\frac{\partial}{\partial z_{ph}}\ln\langle z'|z\rangle|_{z'=z}&=\sum_{g=1}^{N}(\Delta^{>}+z^{\dagger}\Delta^{\circ})_{gp}(\Delta^{\bullet}+\Delta^{>}z+z^{\dagger}\Delta^{>\dagger}+z^{\dagger}\Delta^{\circ}z)^{-1}_{hg}\\
&=[\Lambda^{\bullet-1}(\Delta^{>}+z^{\dagger}\Delta^{\circ})]_{hp}
\end{aligned} \tag{A61}$$

and

$$\nabla_{\mathbf{R}_k}\ln(z,R',P'|z,R,P\rangle|_{R'=R,P'=P}=\mathrm{Tr}\left[\Lambda^{\bullet}(z)^{-1}(I^{\bullet}\quad z^{\dagger})\nabla^{|\rangle}_{\mathbf{R}_k}\Delta\begin{bmatrix}I^{\bullet}\\ z\end{bmatrix}\right] \tag{A62}$$

and also an identical expression for the derivatives with respect to nuclear momenta.

The derivatives of the inverse of the overlap matrix of the occupied dynamic orbitals are similar to Eq. (A11),

$$\frac{\partial}{\partial z_{ph}}[\Lambda^{\bullet}(z)^{-1}]_{mn}=-[\Lambda^{\bullet}(z)^{-1}(\Delta^{>}+z^{\dagger}\Delta^{\circ})]_{mp}[\Lambda^{\bullet}(z)^{-1}]_{hn}\ . \tag{A63}$$

The second derivatives then are

$$\frac{\partial^2\ln\langle z|z\rangle}{\partial z_{qg}\partial z_{ph}}=-[\Lambda^{\bullet}(z)^{-1}(\Delta^{>}+z^{\dagger}\Delta^{\circ})]_{hq}[\Lambda^{\bullet}(z)^{-1}(\Delta^{>}+z^{\dagger}\Delta^{\circ})]_{gp} \tag{A64}$$

and

$$\begin{aligned}
\frac{\partial^2\ln\langle z|z\rangle}{\partial z^*_{qg}\partial z_{ph}}&=\sum_{i=1}^{N}\frac{\partial}{\partial z^*_{qg}}[\Lambda^{\bullet}(z)^{-1}]_{hi}(\Delta^{>}+z^{\dagger}\Delta^{\circ})_{ip}+[\Lambda^{\bullet}(z)^{-1}]_{hg}\Delta^{\circ}_{qp}\\
&=[\Delta^{\circ}-(\Delta^{>\dagger}+\Delta^{\circ}z)\Lambda^{\bullet}(z)^{-1}(\Delta^{>}+z^{\dagger}\Delta^{\circ})]_{qp}[\Lambda^{\bullet}(z)^{-1}]_{hg}
\end{aligned} \tag{A65}$$

or, using the virtual dynamic orbitals v given by Eq. (A56) and the relations (A59),

$$\frac{\partial^2 \ln\langle z|z\rangle}{\partial z^*_{qg}\partial z_{ph}} = [(\Delta^{>\dagger} v^\dagger + \Delta^\circ)\Lambda^\circ(v)^{-1}(v\Delta^{>} + \Delta^\circ)]_{qp}[\Lambda^\bullet(z)^{-1}]_{hg} \ . \tag{A66}$$

To obtain the phase-space metric components Eqs. (3.37) and (3.38), the mixed derivatives are needed with the Thouless parameters and the nuclear positions (momenta). They are

$$\begin{aligned}\frac{\partial}{\partial z'^*}\nabla_{\mathbf{R}_k}\ln\langle z',R'|z,R\rangle|_{z'=z,R'=R} &= (0 \quad I^\circ)\nabla^{|\rangle}_{\mathbf{R}_k}\Delta\begin{bmatrix} I^\bullet \\ z \end{bmatrix}\Lambda^\bullet(z)^{-1} - (\Delta^\vee + \Delta^\circ z)\Lambda^\bullet(z)^{-1}(I^\bullet \quad z^\dagger)\nabla^{|\rangle}_{\mathbf{R}_k}\Delta\begin{bmatrix} I^\bullet \\ z \end{bmatrix}\Lambda^\bullet(z)^{-1} \\ &= (\Delta^\vee v^\dagger + \Delta^\circ)\Lambda^\circ(v)^{-1}(v \quad I^\circ)\nabla^{|\rangle}_{\mathbf{R}_k}\Delta\begin{bmatrix} I^\bullet \\ z \end{bmatrix}\Lambda^\bullet(z)^{-1} = C_{\mathbf{R}_k} \ ,\end{aligned} \tag{A67}$$

where the relations (A59) are again used. The second derivatives with respect to the nuclear positions (momenta) are given by

$$\begin{aligned}\nabla_{\mathbf{R}'_k}\nabla_{\mathbf{R}_l}\ln\langle z',R'|z,R\rangle|_{z'=z,R'=R} = \mathrm{Tr}\Bigg[&\Lambda^\bullet(z)^{-1}(I^\bullet \quad z^\dagger)\nabla^{\langle|}_{\mathbf{R}_k}\nabla^{|\rangle}_{\mathbf{R}_l}\Delta\begin{bmatrix} I^\bullet \\ z \end{bmatrix} \\ &-\Lambda^\bullet(z)^{-1}(I^\bullet \quad z^\dagger)\nabla^{\langle|}_{\mathbf{R}_k}\Delta\begin{bmatrix} I^\bullet \\ z \end{bmatrix}\Lambda^\bullet(z)^{-1}(I^\bullet \quad z^\dagger)\nabla^{|\rangle}_{\mathbf{R}_l}\Delta\begin{bmatrix} I^\bullet \\ z \end{bmatrix}\Bigg] \ .\end{aligned} \tag{A68}$$

d. Density matrix

The one-density of a determinant is the projector on its occupied orbitals (Löwdin, 1955). Therefore

$$\begin{aligned}|\psi\rangle\Gamma\langle\psi| &= |\chi\rangle\begin{bmatrix} I^\bullet & 0 \\ 0 & 0 \end{bmatrix}\langle\chi| \\ &= |\tilde\chi\rangle A\left[A^\dagger\langle\tilde\chi|\begin{bmatrix} I^\bullet & 0 \\ 0 & 0 \end{bmatrix}|\tilde\chi\rangle A\right]^{-1} A^\dagger\langle\tilde\chi| \\ &= |\tilde\chi\rangle\begin{bmatrix} \tilde M & 0 \\ 0 & 0 \end{bmatrix}\langle\tilde\chi| \\ &= |\psi\rangle W^{-1}\tilde Z\begin{bmatrix} \tilde M & 0 \\ 0 & 0 \end{bmatrix}\tilde Z^\dagger W^{\dagger -1}\langle\psi| \\ &= |\phi\rangle\Delta^{-1}\tilde\Gamma\Delta^{-1}\langle\phi| \ ,\end{aligned} \tag{A69}$$

where the transformation matrix A is defined by [see Eqs. (2.33), (2.41), and (A38)]

$$\begin{aligned}\chi &= \psi g = \psi Z X Y h \\ &= \phi W g = \phi\tilde Z U X Y h = \tilde\chi U X Y h = \tilde\chi A\end{aligned} \tag{A70}$$

and M is the inverse overlap matrix of the occupied orbitals before and after the transformation: $M=(I^\bullet + z^\dagger z)^{-1}$ and $\tilde M = \Lambda^\bullet(\tilde z)^{-1}$. Then

$$\begin{aligned}\tilde\Gamma &= \Delta\tilde Z\begin{bmatrix} \tilde M & 0 \\ 0 & 0 \end{bmatrix}\tilde Z^\dagger\Delta \\ &= \Delta\begin{bmatrix} I^\bullet & 0 \\ \tilde z & I^\circ \end{bmatrix}\begin{bmatrix} \tilde M & 0 \\ 0 & 0 \end{bmatrix}\begin{bmatrix} I^\bullet & \tilde z^\dagger \\ 0 & I^\circ \end{bmatrix}\Delta \\ &= \Delta\begin{bmatrix} \tilde M & \tilde M\tilde z^\dagger \\ \tilde z\tilde M & \tilde M\tilde z^\dagger \end{bmatrix}\Delta \\ &= \Delta\begin{bmatrix} I^\bullet \\ \tilde z \end{bmatrix}\tilde M(I^\bullet \quad \tilde z^\dagger)\Delta \ .\end{aligned} \tag{A71}$$

Hence the one-matrix (A16)–(A21) becomes, in the atomic basis,

$$\tilde\Gamma = \Delta\begin{bmatrix} I^\bullet \\ \tilde z \end{bmatrix}\Lambda^\bullet(\tilde z)^{-1}(I^\bullet \quad \tilde z^\dagger)\Delta = \Delta\hat\Gamma\Delta \ . \tag{A72}$$

Notice the overlap matrices on both sides as is typical for projection operators in a nonorthogonal basis. $\hat\Gamma$ is the operator form of the one-matrix, whereas $\tilde\Gamma$ is the matrix element form. It is typical in nonorthogonal bases that every linear operator has two matrices representing it. Here the operator form of the matrix is used and the tilde on the Thouless parameters omitted when no confusion is possible.

Equation (A63) leads to the first derivatives with respect to z^*, again using Eq. (A59),

$$\begin{aligned}\frac{\partial\Gamma_{ij}}{\partial z^*_{ph}} = &\left[\begin{bmatrix} I^\bullet \\ z \end{bmatrix}\Lambda^\bullet(z)^{-1}\right]_{ih} \\ &\times[(\Delta^\vee v^\dagger + \Delta^\circ)\Lambda^\circ(v)^{-1}(v \quad I^\circ)]_{pj} \ .\end{aligned} \tag{A73}$$

Derivatives of the one-density with respect to the nuclear positions (momenta) arise through the dependence on the overlap matrix Δ

$$\begin{aligned}\nabla_{\mathbf{R}_k}\Gamma&=-\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}(I^{\bullet}\;\; z^{\dagger})\nabla_{\mathbf{R}_k}\Delta\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}(I^{\bullet}\;\; z^{\dagger})\\ &=-\Gamma\nabla_{\mathbf{R}_k}\Delta\Gamma\;. \end{aligned}\tag{A74}$$

Note that the total gradient is needed here, and not just through the bra or ket as for the metric components.

The second derivatives with respect to z^* and z then follow, using Eq. (A60),

$$\begin{aligned}\frac{\partial^2\Gamma_{ij}}{\partial z^*_{qg}\partial z_{ph}}=&\left[\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}\right]_{ig}\{[(\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(\Delta^{\circ}+v\Delta^{>})]_{qp}\\ &\times[(\Delta^{\bullet}+\Delta^{>}z)^{-1}(-I^{\bullet}\;\; 0)]_{hj}+[(\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(\Delta^{\circ}+v\Delta^{>})]_{qp}\\ &\times[(\Delta^{\bullet}+\Delta^{>}z)^{-1}(\Delta^{>}+\Delta^{\bullet}v^{\dagger})\Lambda^{\circ}(v)^{-1}(v\;\; I^{\circ})]_{hj}\}\\ &+\left\{-\left[\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}(\Delta^{>}+z^{\dagger}\Delta^{\circ})\right]_{ip}[\Lambda^{\bullet}(z)^{-1}]_{hg}+\begin{bmatrix} 0 \\ I^{\circ} \end{bmatrix}_{ip}[\Lambda^{\bullet}(z)^{-1}]_{hg}\right\}[(\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(v\;\; I^{\circ})]_{qj}\;.\end{aligned}\tag{A75}$$

This expression can be simplified. The 1×2 block matrices in the first two terms can be manipulated using the results from (A59) with the right-hand side Δ replaced by an arbitrary matrix, say A,

$$\begin{aligned}&(-A^{\bullet}+(\Delta^{>}+\Delta^{\bullet}v^{\dagger})\Lambda^{\circ}(v)^{-1}(vA^{\bullet}+A^{\vee})\quad -A^{>}+(\Delta^{>}+\Delta^{\bullet}v^{\dagger})\Lambda^{\circ}(v)^{-1}(vA^{>}+A^{\circ}))\\ &\quad=-((\Delta^{>}z+\Delta^{\bullet})\Lambda^{\bullet}(z)^{-1}(A^{\bullet}+z^{\dagger}A^{\vee})\quad(\Delta^{>}z+\Delta^{\bullet})\Lambda^{\bullet}(z)^{-1}(A^{>}+z^{\dagger}A^{\circ}))\\ &\quad=-(\Delta^{>}z+\Delta^{\bullet})\Lambda^{\bullet}(z)^{-1}(I^{\bullet}\;\; z^{\dagger})A\;.\end{aligned}\tag{A76}$$

Similarly, the 2×1 block matrices in the last two terms can be taken together,

$$\begin{aligned}\begin{bmatrix} A^{>}-(A^{\bullet}+A^{>}z)\Lambda^{\bullet}(z)^{-1}(\Delta^{>}+z^{\dagger}\Delta^{\circ}) \\ A^{\circ}-(A^{\vee}+A^{\circ}z)\Lambda^{\bullet}(z)^{-1}(\Delta^{>}+z^{\dagger}\Delta^{\circ}) \end{bmatrix}&=\begin{bmatrix} (A^{\bullet}v^{\dagger}+A^{>})\Lambda^{\circ}(v)^{-1}(v\Delta^{>}+\Delta^{\circ}) \\ (A^{\vee}v^{\dagger}+A^{\circ})\Lambda^{\circ}(v)^{-1}(v\Delta^{>}+\Delta^{\circ}) \end{bmatrix}\\ &=A\begin{bmatrix} v^{\dagger} \\ I^{\circ} \end{bmatrix}\Lambda^{\circ}(v)^{-1}(v\Delta^{>}+\Delta^{\circ})\;.\end{aligned}\tag{A77}$$

Therefore

$$\begin{aligned}\frac{\partial^2\Gamma_{ij}}{\partial z^*_{qg}\partial z_{ph}}=&-\left[\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}\right]_{ig}[(\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(\Delta^{\circ}+v\Delta^{>})]_{qp}\\ &\times[\Lambda^{\bullet}(z)^{-1}(I^{\bullet}\;\; z^{\dagger})]_{hj}+\left[\begin{bmatrix} v^{\dagger} \\ I^{\circ} \end{bmatrix}\Lambda^{\circ}(v)^{-1}(\Delta^{\circ}+v\Delta^{>})\right]_{ip}\\ &\times[\Lambda^{\bullet}(z)^{-1}]_{hg}[(\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(v\;\; I^{\circ})]_{qj}\;.\end{aligned}\tag{A78}$$

And for the second derivative with respect to z^*, one gets

$$\begin{aligned}\frac{\partial^2\Gamma_{ij}}{\partial z^*_{qg}\partial z^*_{ph}}=&\left[\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}\right]_{ig}\{-[\Delta^{\vee}(\Delta^{\bullet}+z^{\dagger}\Delta^{\vee})^{-1}]_{qh}\\ &+[(\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(\Delta^{\vee}+v\Delta^{\bullet})(\Delta^{\bullet}+z^{\dagger}\Delta^{\vee})^{-1}]_{qh}\}[(\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(v\;\; I^{\circ})]_{pj}\\ &-\left[\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}\right]_{ih}[(\Delta^{\vee}+\Delta^{\circ}z)\Lambda^{\bullet}(z)^{-1}]_{pg}[(\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(v\;\; I^{\circ})]_{qj}\;.\end{aligned}\tag{A79}$$

Again, with the relations from (A59), this simplifies to

$$\frac{\partial^2\Gamma_{ij}}{\partial z^*_{qg}\partial z^*_{ph}} = -\left[\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}\right]_{ig}[(\Delta^{\vee}+\Delta^{\circ}z)\Lambda^{\bullet}(z)^{-1}]_{qh}[(\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(v \quad I^{\circ})]_{pj}$$
$$-\left[\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}\right]_{ih}[(\Delta^{\vee}+\Delta^{\circ}z)\Lambda^{\bullet}(z)^{-1}]_{pg}[(\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(v \quad I^{\circ})]_{qj} \,. \qquad \text{(A80)}$$

The mixed derivatives with respect to electronic parameters and nuclear positions (momenta) follow from (A73)

$$\frac{\partial}{\partial z^*_{ph}}\nabla_{\mathbf{R}_k}\Gamma_{ij} = -\left[\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}(I^{\bullet} \quad z^{\dagger})\nabla_{\mathbf{R}_k}\Delta\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}\right]_{ih}[(\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(v \quad I^{\circ})]_{pj} + \left[\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}\right]_{il}$$
$$\times[(\nabla_{\mathbf{R}_k}\Delta^{\vee}v^{\dagger}+\nabla_{\mathbf{R}_k}\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(v \quad I^{\circ})]_{pj} - \left[\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}\right]_{ih}$$
$$\times\left[(\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(v \quad I^{\circ})\nabla_{\mathbf{R}_k}\Delta\begin{bmatrix} v^{\dagger} \\ I^{\circ} \end{bmatrix}\Lambda^{\circ}(v)^{-1}(v \quad I^{\circ})\right]_{pj} \,. \qquad \text{(A81)}$$

The second derivatives with respect to nuclear positions (momenta) are obtained as

$$\nabla_{\mathbf{R}_k}\nabla_{\mathbf{R}_l}\Gamma = \Gamma\nabla_{\mathbf{R}_k}\Delta\Gamma\nabla_{\mathbf{R}_l}\Delta\Gamma - \Gamma\nabla_{\mathbf{R}_k}\nabla_{\mathbf{R}_l}\Delta\Gamma + \Gamma\nabla_{\mathbf{R}_l}\Delta\Gamma\nabla_{\mathbf{R}_k}\Delta\Gamma \,. \qquad \text{(A82)}$$

e. Energy

The energy of the molecular state is given by Eq. (3.12) with the one-density $\hat{\Gamma}$, Eq. (A72). Only the derivation on the one-electron part is presented for the derivatives. The two-electron part is similar. With (A63), the derivatives of $\mathrm{Tr}(h\Gamma)$ give

$$\frac{\partial E^{(1)}(z^*,z)}{\partial z^*_{ph}} = \left[[-\Delta^{\vee}+\Delta^{\circ}z)\Lambda^{\bullet}(z)^{-1}(h^{\bullet}+z^{\dagger}h^{\vee} \quad h^{>}+z^{\dagger}h^{\circ})+(h^{\vee} \quad h^{\circ})]\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}\right]_{ph} \,. \qquad \text{(A83)}$$

Using relations (A59) with the rightmost Δ replaced by the one-electron integrals h, one finds

$$\frac{\partial E^{(1)}(z^*,z)}{\partial z^*_{ph}} = \left[\left[h^{\vee}\Delta^{\vee}+\Delta^{circ}z)\Lambda^{\bullet}(z)^{-1}(h^{\bullet}+z^{\dagger}h^{\vee}) \quad h^{\circ}-(\Delta^{\vee}+\Delta^{\circ}z)\Lambda^{\bullet}(z)^{-1}(h^{>}+z^{\dagger}h^{\circ})\right]\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}\right]_{ph}$$
$$= \left[\left[(\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(vh^{\bullet}+h^{\vee}) \quad (\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(vh^{>}+h^{\circ})\right]\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}\right]_{ph}$$
$$= \left[(\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(v \quad I^{\circ})h\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}\right]_{ph} \,. \qquad \text{(A84)}$$

With a similar derivation for the two-electron part, the derivatives of the total energy become

$$\frac{\partial E(z^*,z)}{\partial z^*_{ph}} = \left[(\Delta^{\vee}v^{\dagger}+\Delta^{\circ})\Lambda^{\circ}(v)^{-1}(v \quad I^{\circ})F\begin{bmatrix} I^{\bullet} \\ z \end{bmatrix}\Lambda^{\bullet}(z)^{-1}\right]_{ph} \,, \qquad \text{(A85)}$$

with v given by Eq. (A56) and the Fock operator by Eq. (3.23). The derivatives with respect to the nuclear positions (momenta) now contain extra terms involving the gradients of the one-density, which are different from zero in the atomic basis,

$$\nabla_{\mathbf{R}_k}E(z^*,z,R,P) = -\sum_{\substack{l=1 \\ l\neq k}}^{N_{\mathrm{at}}}\frac{Z_kZ_le^2(\mathbf{R}_k-\mathbf{R}_l)}{|\mathbf{R}_k-\mathbf{R}_l|^3} + \mathrm{Tr}(\nabla_{\mathbf{R}_k}h\Gamma) - \mathrm{Tr}(\nabla_{\mathbf{R}_k}\Delta\Gamma h\Gamma)$$
$$+\tfrac{1}{2}\mathrm{Tr}[\mathrm{Tr}(\nabla_{\mathbf{R}_k}V_{ab;ab}\Gamma)_a\Gamma]_b - \mathrm{Tr}[\mathrm{Tr}(\nabla_{\mathbf{R}_k}\Delta\Gamma V_{ab;ab}\Gamma)_a\Gamma]_b \qquad \text{(A86)}$$

and

$$\nabla_{\mathbf{P}_k}E(z^*,z,R,P)=\frac{\mathbf{P}_k}{M_k}+\mathrm{Tr}(\nabla_{\mathbf{P}_k}h\Gamma)-\mathrm{Tr}(\nabla_{\mathbf{P}_k}\Delta\Gamma h\Gamma)+\tfrac{1}{2}\mathrm{Tr}[\mathrm{Tr}(\nabla_{\mathbf{P}_k}V_{ab;ab}\Gamma)_a\Gamma]_b-\mathrm{Tr}[\mathrm{Tr}(\nabla_{\mathbf{P}_k}\Delta\Gamma V_{ab;ab}\Gamma)_a\Gamma]_b\ . \tag{A87}$$

The expressions for parts A and B in Eq. (3.63) for the Hessian are the same as in an orthonormal basis, Eqs. (A32) and (A33), if Eqs. (A72), (A73), (A78), and (A80) are used for the one-particle density and its derivatives. The mixed derivatives F (and G) in Eq. (3.63) have extra terms involving the gradients (A74) of the one-particle density

$$\begin{aligned}\frac{\partial}{\partial z_{ph}^*}\nabla_{\mathbf{R}_k}E(z^*,z,R,P)=&\mathrm{Tr}\left\{[\nabla_{\mathbf{R}_k}h+\mathrm{Tr}(\nabla_{\mathbf{R}_k}V_{ab;ab}\Gamma)_a+\mathrm{Tr}(V_{ab;ab}\nabla_{\mathbf{R}_k}\Gamma)_a]\frac{\partial\Gamma}{\partial z_{ph}^*}\right\}\\&+\mathrm{Tr}\left\{[h+\mathrm{Tr}(V_{ab;ab}\Gamma)_a]\frac{\partial}{\partial z_{ph}^*}\nabla_{\mathbf{R}_k}\Gamma\right\}\ .\end{aligned} \tag{A88}$$

The second derivatives I, J, and K with respect to nuclear positions (momenta) also have extra terms. For example, I becomes

$$\begin{aligned}\nabla_{\mathbf{R}_k}\nabla_{\mathbf{R}_l}E(z^*,z,R,P)=&-\frac{Z_kZ_le^2[3(\mathbf{R}_k-\mathbf{R}_l)(\mathbf{R}_k-\mathbf{R}_l)-|\mathbf{R}_k-\mathbf{R}_l|^2)}{|\mathbf{R}_k-\mathbf{R}_l|^5}\\&+\delta_{kl}\sum_{\substack{n=1\\n\neq 1}}^{N_{\mathrm{at}}}\frac{Z_nZ_le^2[3(\mathbf{R}_n-\mathbf{R}_l)(\mathbf{R}_n-\mathbf{R}_l)-|\mathbf{R}_n-\mathbf{R}_l|^2]}{|\mathbf{R}_n-\mathbf{R}_l|^5}\\&+\mathrm{Tr}\{[\nabla_{\mathbf{R}_k}\nabla_{\mathbf{R}_l}h+\tfrac{1}{2}\mathrm{Tr}(\nabla_{\mathbf{R}_k}\nabla_{\mathbf{R}_l}V_{ab;ab}\Gamma)_a]\Gamma\}+\mathrm{Tr}\{[\nabla_{\mathbf{R}_k}h+\mathrm{Tr}(\nabla_{\mathbf{R}_k}V_{ab;ab}\Gamma)_a]\nabla_{\mathbf{R}_l}\Gamma\}\\&+\mathrm{Tr}\{[\nabla_{\mathbf{R}_l}h+\mathrm{Tr}(\nabla_{\mathbf{R}_l}V_{ab;ab}\Gamma)_a]\nabla_{\mathbf{R}_k}\Gamma\}+\mathrm{Tr}\{[h+\tfrac{1}{2}\mathrm{Tr}(V_{ab;ab}\Gamma)_a]\nabla_{\mathbf{R}_k}\nabla_{\mathbf{R}_l}\Gamma\}\ .\end{aligned} \tag{A89}$$

3. Details of semiempirical approaches

The neglect of diatomic differential overlap (NDDO) approach employs the following approximations (Pople and Beveridge, 1970).

(1) Only the valence electrons are considered explicitly in the calculations. The nucleus and inner-shell electrons are replaced by a fixed-core function. This is the so-called *core approximation* (Zerner, 1972).

(2) A minimal basis set is used; i.e., only atomic orbitals occupied in the atomic ground states are used. This basis set is constructed with Slater-type orbitals. The advantage of using Slater-type orbitals is clarified below. Slater-type orbitals are products of a radial function $R_{nl}(r)$ and a normalized real spherical harmonic $Y_l^m(\theta,\varphi)$, with quantum numbers $\mu=n,l,m$,

$$\begin{aligned}\chi_{nlm}&=R_{nl}(r)Y_l^m(\theta,\varphi)\ ,\\R_{nl}(r)&=\frac{(2\zeta_{nl})^{n+1/2}}{[(2n)!]^{1/2}}r^{n-1}e^{-\zeta_{nl}r}\ ,\end{aligned} \tag{A90}$$

with $l<n$ and $-l\leq m\leq l$. Here ζ_{nl} is referred to as the "orbital exponent" of the Slater-type orbital.

(3) The overlap integrals are neglected. In general, one applies the following relation to all matrix elements,

$$\chi_\mu^A(1)\chi_\nu^B(1)\rightarrow\delta_{AB}\chi_\mu^A(1)\chi_\nu^A(1)\ , \tag{A91}$$

except in the one-electron resonance integrals (one-electron, two-center integrals). Since only valence electrons are considered and Slater-type orbitals are used,

$$\Delta=\begin{bmatrix}\Delta^\bullet & \Delta^>\\ \Delta^\vee & \Delta^\circ\end{bmatrix}=\begin{bmatrix}I^\bullet & 0\\ 0 & I^\circ\end{bmatrix}=I\ ; \tag{A92}$$

i.e., the atomic overlap matrix is approximated by the identity matrix.

(4) The neglect of overlap is consistent with the approximation employed in the two-electron integrals. However, it is important to keep the overlap in the one-electron resonance integrals $\beta_{\mu\nu}$ (one-electron, two-center integrals), since these integrals are responsible for the bonding in molecules

$$\beta_{\mu\nu}=\langle\chi_\mu^A(1)|-\tfrac{1}{2}\nabla_1^2-\sum_A\frac{Z_A}{r_{1A}}|\chi_\nu^B(1)\rangle\ ; \tag{A93}$$

they are treated in the so-called Mulliken approximation, i.e.,

$$\beta_{\mu\nu}=\tfrac{1}{2}(\beta_{\mu_A}+\beta_{\nu_B})\Delta_{\mu_A\nu_B}\ . \tag{A94}$$

(5) Two-electron integrals then become

$$\begin{aligned}&\langle\chi_\mu^A(1)\chi_\nu^B(2)|\chi_\lambda^C(1)\chi_\sigma^D(2)\rangle\\&\quad=\delta_{AB}\delta_{BD}\langle\chi_\mu^A(1)\chi_\nu^B(2)|\chi_\lambda^A(1)\chi_\sigma^B(2)\rangle\ .\end{aligned} \tag{A95}$$

The NDDO model (Pople *et al.*, 1965; Pople and Beveridge, 1970) is considered the lowest level of zero-differential-overlap (ZDO) approach for which there exists a basis set (Parr, 1952; Roby, 1971, 1972). It is properly invariant to local coordinate rotations; so it is not necessary to perform any spherical averaging in integral evaluations over atomic orbitals with angular momentum larger than zero. As a result, unlike the other ZDO models, such as the complete neglect of differential overlap and the intermediate neglect of differential overlap, the NDDO model includes orbital anisotropies. In the Hartree-Fock NDDO method, the computationally dominant step is the diagonalization of the Fock matrix.

Some justifications for the NDDO approximations and their advantages are listed below.

(1) The core approximation in the NDDO model is reasonable because the inner electrons are tightly bound and are, therefore, unlikely to be significantly perturbed by changes in the valence shell. Consequently, most low-energy processes can be accurately described by valence electrons only. Moreover, there is a solid theoretical foundation for the core approximation in terms of an effective Hamiltonian (Freed, 1974).

(2) The use of Slater-type orbitals as building blocks ensures that only short expansions for the molecular orbitals are necessary to give a good description of neutral molecules or positive ions. This justifies the limitation to a minimal basis set. Only in the cases of anions or hypervalent compounds must the atomic basis set be more flexible to accommodate the extra charge density or extra bond(s). Adding diffuse or polarization atomic orbitals is one way of solving this problem. Another is to allow the orbital exponents to vary with the atomic charge. This provides an appropriate description for molecular anions (Iffert and Jug, 1987) and also allows one to keep the minimum basis-set formalism. The use of Slater-type orbitals is convenient in the gradient calculation, because the differentiation of a Slater-type-orbital function with respect to a nuclear coordinate can be expressed in terms of Slater-type orbitals, except at the edges of the table of quantum numbers

$$\frac{d}{dx_i}\chi_{nlm}=\sum_m C^{i1}_{nlm}\chi_{n-1,l-1,m}+\sum_m C^{i2}_{nlm}\chi_{n-1,l+1,m}+\sum_m C^{i3}_{nlm}\chi_{n,l+1,m}+\sum_m C^{i4}_{nlm}\chi_{n,l-1,m} \tag{A96}$$

if $\chi_{nlm}\equiv 0$ is defined for $n\leq 0$ or $l<0$ and

$$\chi_{nnm}\equiv\chi_{n+1,nm}/r\propto r^{n-1}Y_{nm}e^{-\zeta_{nn}r}\,. \tag{A97}$$

Higher derivatives of Slater-type orbitals are again expressible in terms of Slater-type orbitals and additional "edge" functions.

(3) It can be shown (Rüdenberg, 1951; Löwdin, 1953) that the approximation of the two-electron integrals by the NDDO is correct up to second order in the overlap expansion. It is also possible to evaluate the three- and four-center integrals in terms of overlap and two-center integrals (Löwdin, 1953). However, if the two-electron integrals are parametrized with respect to experimental data, the errors caused by neglecting the three- and four-center integrals can be minimized.

Caution must be exercised when considering the derivatives of the atomic-orbital overlap Δ with respect to the nuclear position. If the NDDO approximation is made for the overlap, that is $\Delta=I$, then taking the derivative yields no contribution. This does not mean that C_R equation (3.37) and C_{RR} equation (3.38) vanish, since these involve bra-ket derivatives of the overlap and depend on the basis changing, not just the overlap matrix. This is consistent with the *ab initio* END equations, as it must, since the NDDO approximation should not affect the proper coupling between electrons and nuclei. Consequently, the derivative of the nonapproximated atomic-orbital overlap is first taken, and then the NDDO approximation is performed on the resulting expression.

The Austin Model 1 (AM1) approach to the NDDO approximation (Dewar *et al.*, 1985) has been extensively tested and has been shown to reproduce geometry, heats of formation, dipole moments, and ionization potentials very well (Dewar *et al.*, 1985; Thiel, 1988; Stewart, 1990). In addition, the overall performance of the AM1 for computing molecular properties (excitation energies, vibrational frequencies, and intensities) and quantities relevant for chemical reactions (enthalpy of reaction and activation energies) is quite satisfactory (Stewart, 1990). Thus it seems appropriate to use the AM1 formulation of the NDDO method in a time-dependent treatment. Results for dynamical properties like intra- and intermolecular charge transfer, transition-state spectroscopy, photodissociation, etc., can be used to check the performance of the time-dependent AM1 method. Extensions of this approach can be implemented, where the parametrization would also include experimental dynamical properties in the data base.

The definition of the Fock matrix elements in the AM1 model is (Dewar and Thiel, 1977; Dewar *et al.*, 1985; Stewart, 1990)

(1) diagonal terms

$$F_{\mu_A\mu_A}=U_{\mu_A\mu_A}-\sum_{B\neq A}Z_B(\mu_A\mu_A|s_Bs_B)+\sum_{\nu_A}\Gamma_{\nu_A\nu_A}[(\mu_A\mu_A|\nu_A\nu_A)-\tfrac{1}{2}(\mu_A\nu_A|\mu_A\nu_A)]+\sum_{B\neq A}\sum_{\lambda_B}\sum_{\sigma_B}\Gamma_{\lambda_B\sigma_B}(\mu_A\mu_A|\lambda_B\sigma_B)\,, \tag{A98}$$

(2) off-diagonal terms on the same atom

$$F_{\mu_A\nu_A}=-\sum_{B\neq A}Z_B(\mu_A\nu_A|s_Bs_B)+\tfrac{1}{2}\Gamma_{\mu_A\nu_A}[3(\mu_A\nu_A|\mu_A\nu_A)-(\mu_A\mu_A|\nu_A\nu_A)]+\sum_{B\neq A}\sum_{\lambda_B}\sum_{\sigma_B}\Gamma_{\lambda_B\sigma_B}(\mu_A\nu_A|\lambda_B\sigma_B)\,, \tag{A99}$$

(3) general terms on different atoms

$$F_{\mu_A\lambda_B}=\tfrac{1}{2}(\beta_{\mu_A}+\beta_{\lambda_B})\Delta_{\mu_A\lambda_B}-\tfrac{1}{2}\sum_{\nu_A}\sum_{\sigma_B}\Gamma_{\mu_A\lambda_B}(\mu_A\lambda_B|\nu_A\sigma_B)\,, \tag{A100}$$

where μ_A, ν_A (λ_B, σ_B) are atomic orbitals centered in A (B), and $\Gamma_{\mu\lambda}$ is the one-density or "bond order" matrix.

In order to complete the definition of the AM1 model, expressions or numbers are needed for each one of the terms that go into the elements of the Fock matrix. That is, (1) $U_{\mu_A\mu_A}$ are one-center, one-electron terms and are parametrized from spectroscopic data for valence states of atom A and its ions; (2) Z_A is the atomic number of atom A *minus* the number of core electrons; (3) the nuclear repulsion energy is given by

$$E_{AB}=Z_AZ_B\langle s_As_A|s_Bs_B\rangle+\frac{Z_AZ_B}{R_{AB}}\sum_{i=1}^{4}[a_i^Ae^{-b_i^A(R_{AB}-c_i^A)^2}+a_i^Be^{-b_i^B(R_{AB}-c_i^B)^2}] \tag{A101}$$

where a_i^X, b_i^X, and c_i^X are fitted parameters; (4) the β_μ are determined by fitting results of the AM1 model to experimental data that are related to bonding in molecules, like heat of formation, geometries, dipole moments, ionization potentials, etc.; (5) the repulsion integrals are expanded in terms of multipoles M_{lm} and are approximated by

$$(\mu_A\nu_A|\lambda_B\sigma_B)=\sum_{l_1=0}^{\infty}\sum_{l_2=0}^{\infty}\sum_{m=-l_{\min}}^{l_{\min}}\left[\left(\frac{1}{2^{l_1+l_2}}\right)\sum_{i=1}^{l_1}\sum_{j=1}^{l_2}\frac{1}{\sqrt{R_{ij}^2+(\rho_{l_1}^A+\rho_{l_2}^B)^2}}\right], \tag{A102}$$

where

$$R_{ij}=R_{AB}+\eta_{l_1}^AD_1^A+\eta_{l_1}^BD_1^B+\eta_{l_2}^AD_2^A+\eta_{l_2}^BD_2^B \tag{A103}$$

with $\eta=\ldots,\pm2,\pm1,0$ depending upon the order of the dipole, and ρ and D are derived parameters, that is, $D=D(\zeta_\mu)$ and $\rho=\rho(U_{\mu\nu},D)$. In the case of a minimum *sp* basis set, there are 22 distinct repulsion integrals. The inclusion of *d* orbitals increases this number to 450, which makes this type of approximation for the repulsion integrals cumbersome when extended beyond the *sp* basis.

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