

General Born–Oppenheimer–Huang approach to systems of electrons and nuclei

Roi Baer Donald J. Kouri Michael Baer David K. Hoffman

Citation: **119**, 6998 (2003); doi: 10.1063/1.1606433

View online: <http://dx.doi.org/10.1063/1.1606433>

View Table of Contents: <http://aip.scitation.org/toc/jcp/119/14>

Published by the [American Institute of Physics](#)

COMPLETELY

REDESIGNED!



**PHYSICS
TODAY**

Physics Today Buyer's Guide
Search with a purpose.

ARTICLES

General Born–Oppenheimer–Huang approach to systems of electrons and nuclei

Roi Baer

*Department of Physical Chemistry and Lise Meitner Center for Computational Quantum Chemistry, Hebrew University of Jerusalem, Jerusalem, 91904, Israel*Donald J. Kouri^{a)}*Departments of Chemistry, Mathematics, and Physics, University of Houston, Houston, Texas 77204-5003*Michael Baer^{b)}*Department of Chemistry, University of Houston, Houston, Texas 77204-5003*

David K. Hoffman

Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011

(Received 20 February 2003; accepted 15 July 2003)

We reconsider the Born–Oppenheimer–Huang treatment of systems of electrons and nuclei for the case of their interaction with time-dependent fields. Initially, we present a framework in which all expressions derived are formally exact since no truncations are introduced. The objective is to explore the general structure of the equations under the most unrestricted conditions, including the possibility that the electronic basis is dependent both on the nuclear coordinates and on time. We then derive an application of the theory applicable to cases of interaction with strong time-dependent fields. The method truncates the electronic basis only after the time-dependent interaction is taken into account in the electronic wave functions. This leads to theory which is similar to a Born–Oppenheimer-type truncation within the interaction picture. © 2003 American Institute of Physics. [DOI: 10.1063/1.1606433]

I. INTRODUCTION

The Born–Oppenheimer–Huang (BOH) treatment of systems of electrons and nuclei has long been used for the description of quantum dynamics in atomic, molecular and chemical physics.^{1–16} Usually one either immediately separates the explicit time dependence to consider stationary states of total energy \mathbf{E} , or one assumes that all of the time dependence is contained in the nuclear wave function. The traditional BOH treatment restricts the adiabatic electronic wave functions to having no explicit time dependence. This need not be so as has been mentioned elsewhere,⁶ though, intuitively, introducing time-dependent electronic states seems a needless complication. However, it is interesting to explore the most general form that the equations can have rather than imposing restrictions from the outset on the manner in which the time dependence enters. We shall see that doing so leads to a description that has interesting parallels with the situation of charged particles in the presence of an electromagnetic field. In particular, we find that the natural connection can be viewed from the standpoint of various interaction pictures, the transformations which behave like gauge transformation giving rise to gauge contributions to

the nuclear momentum.¹⁷ In general, one finds that it is crucial that the momentum operator of the nuclei includes all possible contributions just as is the case for a charged particle in a vector potential.

This paper is organized as follows: In Sec. II we present the formal analysis based on the nonrelativistic Schrödinger equation for a system of nuclei and electrons. Section III contains a discussion of the results.

II. GENERAL TIME-DEPENDENT TREATMENT OF COMBINED NUCLEAR AND ELECTRON DYNAMICS

We consider a molecular system with N nuclei and some number of electrons, which we treat using a direct product basis. For notational convenience we incorporate the electronic degrees of freedom for the state of the system using an abstract set of vectors, and we treat the nuclear degrees of freedom in the coordinate representation. The identity in this “semiabstract” form is

$$\hat{1} = \sum_j |j, \mathbf{R}, t; \lambda\rangle \delta(\mathbf{R} - \mathbf{R}) \langle j, \mathbf{R}, t; \lambda|. \quad (1)$$

The index λ is used to denote the particular choice of electronic basis (to differentiate among the infinitely many possibilities) and j indicates a particular member of the electronic basis set λ . Here \mathbf{R} represents the complete set of nuclear coordinates. For notational convenience the abstract vectors have been written as though they are discretely in-

^{a)}Electronic mail: kouri@uh.edu

^{b)}Author to whom correspondence should be addressed. Permanent address: Soreq Nuclear Research Center, Yavne 81800, Israel. Electronic mail: michaelb@fh.huji.ac.il

dexed, but this need not be the case. Note that we allow for the possibility of using a different set of abstract vectors at each \mathbf{R} and t and that we have indicated this flexibility explicitly. The semiabstract form of a general system operator, $\hat{\mathbf{O}}$, is

$$\hat{\mathbf{O}}(\mathbf{R}|\mathbf{R}') = \sum_j \sum_k |j, \mathbf{R}, t; \lambda\rangle \mathbf{O}(\mathbf{R}|\mathbf{R}')_{j,k}^{(\lambda)} \langle k, \mathbf{R}', t; \lambda|, \quad (2)$$

where

$$\begin{aligned} \mathbf{O}(\mathbf{R}|\mathbf{R}')_{j,k}^{(\lambda)} &= \langle j, \mathbf{R}, t; \lambda | \hat{\mathbf{O}}(\mathbf{R}|\mathbf{R}') | k, \mathbf{R}', t; \lambda \rangle \\ &= [\underline{\underline{\mathbf{O}(\mathbf{R}|\mathbf{R}')}}]_{j,k}^{(\lambda)}, \end{aligned} \quad (3)$$

is a matrix element in the λ , \mathbf{R} representation. The double underline indicates a matrix in the electronic basis quantum numbers. In particular, the matrix element for the operator $\hat{\mathbf{P}}_n$, corresponding to the linear momentum operator of nucleus n , is

$$\begin{aligned} \mathbf{P}_n(\mathbf{R}|\mathbf{R}')_{j,k}^{(\lambda)} &= \langle j, \mathbf{R}, t; \lambda | \hat{\mathbf{P}}_n(\mathbf{R}|\mathbf{R}') | k, \mathbf{R}', t; \lambda \rangle \\ &= \frac{\hbar}{i} \langle j, \mathbf{R}, t; \lambda | \nabla_n \delta(\mathbf{R} - \mathbf{R}') | k, \mathbf{R}', t; \lambda \rangle \\ &= \left\{ \frac{\hbar}{i} \nabla_n + \underline{\underline{\varphi_n(\mathbf{R}, t)}} \right\}_{j,k}^{(\lambda)} \delta(\mathbf{R} - \mathbf{R}'), \end{aligned} \quad (4)$$

where ∇_n is the gradient with respect to the coordinates of nucleus n , and, by definition

$$\varphi_n(\mathbf{R}, t)_{j,k}^{(\lambda)} \equiv \frac{\hbar}{i} \langle j, \mathbf{R}, t; \lambda | \nabla_n | k, \mathbf{R}, t; \lambda \rangle. \quad (5)$$

From the orthogonality of the electronic ket vectors it is immediate seen that $\varphi_n(\mathbf{R}, t)_{j,k}^{(\lambda)}$ is a self-adjoint matrix. Thus, the linear momentum matrix element in this representation is split into two contributions (neither of which is *a priori* small) that are determined by the choice of representation, λ . This immediately shows the parallel between the present system and a charged particle in an external electromagnetic field. Specifically, there is a contribution to the momentum of nucleus n that arises due to the incomplete separation of electronic and nuclear degrees of freedom; i.e., the electronic basis states can, in general, depend on both the nuclear coordinates and time. We remark that different choices of the electronic basis correspond to various interaction pictures and the related unitary or gague-like transformations. The j th component of the wave function in the λ , \mathbf{R} representation is given by

$$\psi(\mathbf{R}, t)_j^{(\lambda)} = \langle j, \mathbf{R}, t; \lambda | \psi(\mathbf{R}, t) \rangle, \quad (6)$$

where $|\psi(\mathbf{R}, t)\rangle$ is the state of the system in its original, semiabstract form. If one interprets $\psi(\mathbf{R}, t)^{(\lambda)}$ as the nuclear wave function, then clearly $(\hbar/i)\nabla_n$ acting on it is not the total momentum. It lacks the contribution arising from the gauge transformation, which is associated with the nuclear position dependence of the electronic basis. The transformation between representations λ_0 and λ_1 is conveniently represented in matrix notation as follows:

$$\underline{\underline{\psi(\mathbf{R}, t)^{(\lambda_1)}}} = \underline{\underline{\mathbf{A}_{\lambda_0 \rightarrow \lambda_1}(\mathbf{R})}} \cdot \underline{\underline{\psi(\mathbf{R}, t)^{(\lambda_0)}}}, \quad (7)$$

where the matrix $\underline{\underline{\mathbf{A}_{\lambda_0 \rightarrow \lambda_1}(\mathbf{R})}}$ is defined by

$$[\underline{\underline{\mathbf{A}_{\lambda_0 \rightarrow \lambda_1}(\mathbf{R})}}]_{j,k} = \langle j, \mathbf{R}, t; \lambda_1 | k, \mathbf{R}, t; \lambda_0 \rangle. \quad (8)$$

It is unitary (and can be interpreted as a gauge transformation) satisfying the conditions

$$[\underline{\underline{\mathbf{A}_{\lambda_0 \rightarrow \lambda_1}(\mathbf{R})}}]^{-1} = [\underline{\underline{\mathbf{A}_{\lambda_0 \rightarrow \lambda_1}(\mathbf{R})}}]^\dagger = \underline{\underline{\mathbf{A}_{\lambda_1 \rightarrow \lambda_0}(\mathbf{R})}}. \quad (9)$$

For a general semiabstract operator $\hat{\mathbf{O}}(\mathbf{R}|\mathbf{R}')$, the *mixed-representation* matrix element

$$\langle j, \mathbf{R}, t; \lambda_1 | \hat{\mathbf{O}}(\mathbf{R}|\mathbf{R}') | k, \mathbf{R}', t; \lambda_0 \rangle, \quad (10)$$

can be analyzed in two different ways; one can insert a resolution of the identity either in front of or following the operator, to obtain the identity

$$\underline{\underline{\mathbf{O}(\mathbf{R}|\mathbf{R}')^{(\lambda_1)}}} \cdot \underline{\underline{\mathbf{A}_{\lambda_0 \rightarrow \lambda_1}(\mathbf{R}')}} = \underline{\underline{\mathbf{A}_{\lambda_0 \rightarrow \lambda_1}(\mathbf{R})}} \cdot \underline{\underline{\mathbf{O}(\mathbf{R}|\mathbf{R}')^{(\lambda_0)}}}. \quad (11)$$

In particular for $\underline{\underline{\varphi_n(\mathbf{R}, t)}}$ we find that

$$\begin{aligned} \frac{\hbar}{i} \nabla_n \underline{\underline{\mathbf{A}_{\lambda_0 \rightarrow \lambda_1}(\mathbf{R})}} + \underline{\underline{\varphi_n(\mathbf{R}, t)^{(\lambda_1)}}} \cdot \underline{\underline{\mathbf{A}_{\lambda_0 \rightarrow \lambda_1}(\mathbf{R})}} \\ = \underline{\underline{\mathbf{A}_{\lambda_1 \rightarrow \lambda_0}(\mathbf{R})}} \cdot \underline{\underline{\varphi_n(\mathbf{R}, t)^{(\lambda_0)}}}. \end{aligned} \quad (12)$$

This can be interpreted as the gauge transformation of the momentum operator for nucleus n arising due to the transformation from the λ_0 to the λ_1 pictures.

We now consider a general electronic basis. The equation for the time-dependent nuclear wave function, $\psi(\mathbf{R}, t)_j^{(\lambda)}$, is derived starting from the time-dependent Schrödinger equation

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \left\{ \sum_k |k, \mathbf{R}, t; \lambda\rangle \psi(\mathbf{R}, t)_k^{(\lambda)} \right\} \\ = \int d\mathbf{R}' \hat{\mathbf{H}}(\mathbf{R}|\mathbf{R}') \sum_k |k, \mathbf{R}', t; \lambda\rangle \psi(\mathbf{R}', t)_k^{(\lambda)}, \end{aligned} \quad (13)$$

where $\hat{\mathbf{H}}(\mathbf{R}|\mathbf{R}')$ is the semiabstract Hamiltonian operator. Thus

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \psi(\mathbf{R}, t)_j^{(\lambda)} &= \sum_k \left[\int d\mathbf{R}' \sum_{n=1}^N \frac{\langle j, \mathbf{R}; \lambda | \hat{\mathbf{P}}_n^2(\mathbf{R}|\mathbf{R}') | k, \mathbf{R}'; \lambda \rangle}{2m_n} \psi(\mathbf{R}', t)_k^{(\lambda)} \right] \\ &+ \langle j, \mathbf{R}, t; \lambda | \left(\mathbf{H}_e(\mathbf{R}, t) - i\hbar \frac{\partial}{\partial t} \right) | k, \mathbf{R}, t; \lambda \rangle \psi(\mathbf{R}, t)_k^{(\lambda)}. \end{aligned} \quad (14)$$

Here we have written the Hamiltonian in the form

$$\hat{\mathbf{H}}(\mathbf{R}|\mathbf{R}') = \sum_{n=1}^N \frac{\hat{\mathbf{P}}_n^2(\mathbf{R}|\mathbf{R}')}{2m_n} + \delta(\mathbf{R}-\mathbf{R}')\hat{\mathbf{H}}_e(\mathbf{R},t),$$

where the electronic Hamiltonian, $\hat{\mathbf{H}}_e(\mathbf{R},t)$, is given in terms of $\hat{\mathbf{T}}_e$ and $\hat{\mathbf{V}}(\mathbf{R},t)$, respectively, the kinetic-energy operator for the electrons and the system potential energy operator, by

$$\hat{\mathbf{H}}_e(\mathbf{R},t) = \hat{\mathbf{T}}_e + \hat{\mathbf{V}}(\mathbf{R},t). \quad (15)$$

Note that we have allowed explicitly for the possibility that $\hat{\mathbf{V}}$ can be time-dependent. From Eq. (4) we find that

$$\begin{aligned} \langle j, \mathbf{R}, t; \lambda | \hat{\mathbf{P}}_n^2(\mathbf{R}|\mathbf{R}') | k, \mathbf{R}', t; \lambda \rangle \\ = \int d\mathbf{R}'' \sum \langle j, \mathbf{R}, t; \lambda | \hat{\mathbf{P}}_n(\mathbf{R}|\mathbf{R}'') | l, \mathbf{R}'', t; \lambda \rangle \\ \times \langle l, \mathbf{R}'', t; \lambda | \hat{\mathbf{P}}_n(\mathbf{R}''|\mathbf{R}') | k, \mathbf{R}', t; \lambda \rangle \end{aligned} \quad (16)$$

$$= \left[\left\{ \frac{\hbar}{i} \nabla_n + \underline{\varphi}_n(\mathbf{R}, t)^{(\lambda)} \right\}^2 \right]_{jk} \delta(\mathbf{R}-\mathbf{R}'), \quad (17)$$

and thus

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \psi(\mathbf{R}, t)_j^{(\lambda)} = \sum_k \left[\sum_{n=1}^N \frac{1}{2m_n} \left\{ \frac{\hbar}{i} \nabla_n + \underline{\varphi}_n(\mathbf{R}, t)^{(\lambda)} \right\}^2 \right]_{jk} \\ + \langle j, \mathbf{R}, t; \lambda | \left(\hat{\mathbf{H}}_e(\mathbf{R}, t) - i\hbar \frac{\partial}{\partial t} \right) | k, \mathbf{R}, t; \lambda \rangle \\ \times \psi(\mathbf{R}, t)_k^{(\lambda)}. \end{aligned} \quad (18)$$

This equation constitutes a general result for the time-dependent problem and is the central result of this paper. It is in this form that the connection between the electronic basis choice λ , the choice of interaction picture, and the choice of gauge is most apparent. Essentially, one chooses a basis λ by deciding what result is desired when $[\hat{\mathbf{H}}_e(\mathbf{R}, t) - i\hbar \partial/\partial t]$ acts on the electronic state vectors $|k, \mathbf{R}, t; \lambda\rangle$. This also determines the particular interaction picture, and when the $|k, \mathbf{R}, t=0; \lambda\rangle$'s are *eigenstates* of $\hat{\mathbf{H}}_e(\mathbf{R}, t)$ it is clear that the time dependence of the states $|k, \mathbf{R}, t; \lambda\rangle$ is simply a phase factor (which depends on \mathbf{R}). That is, it is obviously simply a gauge transformation of the electronic state. Of course there are many choices that can be made. We consider one of these (which differs significantly from the ordinary approach) which shows explicitly the power of the present general formulation.

The electronic adiabatic basis set ($\lambda = AD$) is chosen so that its members satisfy the time-dependent Schrödinger equation for the electronic problem, that is

$$\left(\hat{\mathbf{H}}_e(\mathbf{R}, t) - i\hbar \frac{\partial}{\partial t} \right) |k, \mathbf{R}, t; AD\rangle = 0. \quad (19)$$

From Eq. (18) the equation for $\psi(\mathbf{R}, t)_j^{(AD)}$ then is

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \psi(\mathbf{R}, t)_j^{(AD)} \\ = \sum_k \left[\sum_{n=1}^N \frac{1}{2m_n} \left\{ \frac{\hbar}{i} \nabla_n + \underline{\varphi}_n(\mathbf{R}, t)^{(AD)} \right\}^2 \right]_{jk} \\ \times \psi(\mathbf{R}, t)_k^{(AD)}. \end{aligned} \quad (20)$$

Note that $\hat{\mathbf{V}}(t)$ does not appear explicitly in the final equation. We shall refer to this as the “dressed nuclei” gauge because there is no longer any nuclear potential, but rather the nuclei possess momentum that consists of contributions $\frac{\hbar}{i} \nabla_n$ and $\underline{\varphi}_n(\mathbf{R})^{(AD)}$. It is the fact that the $\psi(\mathbf{R}, t)_{j,k}^{(\lambda)}$ do *not* carry all of the nuclear coordinate dependence which causes the gradient operator to no longer be the total momentum operator.

As an application of this development, which allows great flexibility in choosing the underlying gauge, we consider the problem of a nonperturbative interaction of a molecule with a strong electromagnetic field. Assuming that $\hat{\mathbf{V}}(t) = \mathbf{V}_{eN} + \mathbf{E}(t) \cdot \hat{\mathbf{D}}$ where \mathbf{V}_{eN} is the electron–nucleus Coulomb interaction and $\hat{\mathbf{D}} = e \sum_n \hat{\mathbf{r}}_n$ is the total electronic dipole moment and $\mathbf{E}(t)$ is the electric field at time t . We assume the electric field is turned on at time $t > 0$. Let us expand the M time-dependent adiabatic functions as a linear combination of L eigenstates at $t=0$ (i.e., the time-independent adiabatic basis):

$$\begin{aligned} |j, \mathbf{R}, t; AD\rangle = \sum_{l=1}^L |l, \mathbf{R}, t=0; AD\rangle \omega_{lj}(t, \mathbf{R}); \\ j = 1, 2, \dots, M. \end{aligned} \quad (21)$$

It is important to realize that ω is a rectangular matrix of dimension $L \times M$ and that in actual applications L may be considerably *larger* than M without affecting the number of coupled time-dependent Schrödinger equations one has to solve (which is L).

This approach dresses the low (M) dimensional time-dependent electronic problem using a (much) larger (L -) dimensional space of time-independent adiabatic wave functions. This is in contradiction to the usual approach that uses a small L to start with (in order to keep the number of Schrödinger equations, to be solved, as small as possible) and, therefore, may distort the effect of the perturbation, in particular when the perturbation is large.

This inspires a new transformation, where the $\varphi_n(\mathbf{R}, t)$ which is a $M \times M$ matrix from Eq. (5) can be shown to be given in the form:

$$\varphi_n^{(DRA)}(\mathbf{R}, t) = \underline{\omega}^\dagger(\mathbf{R}, t) \cdot \left(\frac{\hbar}{i} \nabla + \underline{\varphi}_n(\mathbf{R}, t=0) \right) \cdot \underline{\omega}(\mathbf{R}, t), \quad (22)$$

where $\varphi_n(\mathbf{R}, t=0)$ is a matrix of dimension of $L \times L$. Here, “DRA” denotes the “dressed adiabatic” representation. The dressed nuclear equation of motion is of reduced number of effective electronic states (i.e., M) is

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{R}, t)_j^{(\text{DRA})} = \sum_k \left[\sum_{n=1}^N \frac{1}{2m_n} \left\{ \frac{\hbar}{i} \nabla_n + \wp_n(\mathbf{R}, t)^{(\text{DRA})} \right\}^2 \right]_{j,k} \times \psi(\mathbf{R}, t)_k^{(\text{DRA})}. \quad (23)$$

This equation can be diabaticized, by carrying out a time-dependent adiabatic-to-diabatic transformation (similar to the one performed within the time-independent framework—see Ref. 3) employing the matrix $\underline{\mathbf{A}}_{\text{DRA} \rightarrow \text{DRD}}(\mathbf{R}, t)$ which has to be a solution of the space–time first-order differential equation:

$$\frac{\hbar}{i} (\nabla_n + \underline{\wp}_n(\mathbf{R}, t)^{(\text{DRA})}) \underline{\mathbf{A}}_{\text{DRA} \rightarrow \text{DRD}}(\mathbf{R}, t) = 0, \quad (24)$$

$$i\hbar \left(\frac{\partial}{\partial t} + \underline{\mathbf{H}}_e(\mathbf{R}, t)^{(\text{DRA})} \right) \underline{\mathbf{A}}_{\text{DRA} \rightarrow \text{DRD}}(\mathbf{R}, t) = 0,$$

where the dressed adiabatic $M \times M$ potential matrix $\underline{\mathbf{H}}_e(\mathbf{R}, t)^{\text{DRA}}$ is

$$\underline{\mathbf{H}}_e^{\text{DRA}}(\mathbf{R}, t) = \underline{\omega}^\dagger(\mathbf{R}, t) \underline{\omega}(\mathbf{R}, t) = \underline{\omega}^\dagger(\mathbf{R}, t) \underline{\mathbf{H}}_e^{\text{DRA}}(\mathbf{R}, t=0) \underline{\omega}(\mathbf{R}, t). \quad (25)$$

It is important to realize that the dimensions of $\underline{\omega}^\dagger$, $\underline{\mathbf{H}}_e(\mathbf{R}, t=0)^{\text{DRA}}$ and $\underline{\omega}$ are $M \times L$, $L \times L$, and is $L \times M$, respectively. The final set of coupled nuclear Schrödinger equations is

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{R}, t)_j^{(\text{DRD})} = \sum_{n=1}^N \frac{1}{2m_n} \left\{ \frac{\hbar}{i} \nabla_n \right\}^2 \psi(\mathbf{R}, t)_j^{(\text{DRD})} + \sum_k [\underline{\mathbf{H}}_e(\mathbf{R}, t)]_{j,k}^{(\text{DRD})} \psi(\mathbf{R}, t)_k^{(\text{DRD})}, \quad (26)$$

where the dressed-diabatic $M \times M$ potential matrix is

$$\underline{\mathbf{H}}_e^{\text{DRD}}(\mathbf{R}, t) = \underline{\mathbf{A}}_{\text{DRA} \rightarrow \text{DRD}}^\dagger(\mathbf{R}, t) \cdot \underline{\mathbf{H}}_e^{\text{DRA}}(\mathbf{R}, t) \cdot \underline{\mathbf{A}}_{\text{DRA} \rightarrow \text{DRD}}(\mathbf{R}, t). \quad (27)$$

It is important to emphasize that a solution for Eq. (24) is guaranteed only in case the time–space curl condition (similar to the one encountered in the time-independent framework^{3,16}) is fulfilled. The solution follows by integrating Eqs. (24) along a *time–space* contours.

III. DISCUSSION

We have seen that the most general treatment of the time-dependent Schrödinger equation describing systems of nuclei and electrons leads to equations which, like those of a charge particle in an external vector potential, involve contributions to nuclear momentum operator in addition to \hbar/i times the nuclear gradient operator. In the present instance, such nuclear momentum terms result from the fact that the nuclear “wave functions” $\psi(\mathbf{R}, t)_k^{(\lambda)}$ do *not* contain all of the dependence on the nuclear coordinates. The structure is such

that different choices of the electronic basis essentially can be viewed as invoking different interaction pictures, or equivalently different gauges.

We also suggest that there is an analogy with the centrifugal potential and centrifugal reaction in rotational motion. For a central force problem, the motion of a particle in three dimensions can be reduced to an equivalent one-dimensional problem. The radial part of the true kinetic energy becomes the kinetic energy of the one-dimensional problem, while the rotational part of the true kinetic energy is interpreted as an additional contribution to the potential energy for the one-dimensional motion. It in turn gives rise, classically, to a fictitious force. Analogously for our problem, the true kinetic-energy operator for the nuclei is

$$\sum_{n=1}^N \frac{\hat{P}_n^2}{2m_n},$$

where in the λ, R representation the momentum operator is given by Eq. (4). If, in the spirit of the Born–Oppenheimer development, one chooses to interpret the components of $\underline{\psi}(\mathbf{R}, t)^{(\lambda)}$ as nuclear wave functions and correspondingly $(-\hbar^2/2m_n)\nabla_n^2$ as the nuclear kinetic-energy operator for particle n , then the terms that arise from $\wp_n(\mathbf{R})^{(\lambda)}$ in the true kinetic energy are no longer to be interpreted as nuclear kinetic-energy terms. However, they are still a part of the Hamiltonian, of course, and thus must be ultimately reintroduced in a different guise. The effects of the electrons on the nuclear dynamics can thus be viewed as leading to fictitious nuclei (i.e., dressed nuclei) whose dynamics is “potential free.”

As an application to the theory, we have presented a method to treat the nuclear dynamics under strong electromagnetic fields. The treatment proposed includes the projection of the fully time-dependent states at time t on the adiabatic states at time $t=0$ (before the field is turned on). Only then a truncation to a smaller basis is performed, where the nuclear dynamics is carried out. This approach is strictly different from the methods in common use, where the time-dependent perturbation is represented as a truncated matrix at the level of the $t=0$ adiabatic states. One way to understand our approach is that while the conventional approaches truncate the equations of the Schrödinger picture, we advocate the truncation of the “dressed” equations within the interaction (or Dirac) picture. This should lead to a considerably better description of the nuclear dynamics using similar computing resources.

ACKNOWLEDGMENTS

Supported in part by National Science Foundation Grant No. CHE-0074311; R. A. Welch Foundation Grant No. E-0608; Texas Learning and Computation Center, University of Houston; Institute for Digital Informatics and Analysis, University of Houston. Supported in part by National Science Foundation Grant No. CHE-0074311 and the Department of Chemistry, University of Houston. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Grant No. 2-7405-ENG82.

- ¹M. Born and J. R. Oppenheimer, *Ann. Phys. (Leipzig)* **84**, 457 (1927).
- ²M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954).
- ³M. Baer, *Chem. Phys. Lett.* **35**, 112 (1975); *Mol. Phys.* **40**, 1011 (1980).
- ⁴C. A. Mead and D. G. Truhlar, *J. Chem. Phys.* **70**, 2284 (1979).
- ⁵M. V. Berry, *Proc. R. Soc. London* **A392**, 45 (1984).
- ⁶M. Baer, in *The Role of Degenerate States in Chemistry*, edited by M. Baer and G. D. Billing (Wiley, Hoboken, N.J.), *Adv. Chem. Phys.* **124**, 39 (2002); S. Adhikiri and G. D. Billing, *ibid.* **124**, 143 (2002); R. Englman and A. Yahalom, *ibid.* **124**, 197 (2002); A. Kuppermann and R. Abrol, *ibid.* **124**, 283 (2002).
- ⁷R. Abrol, A. Shaw, A. Kuppermann, and D. R. Yarkony, *J. Chem. Phys.* **115**, 4640 (2001).
- ⁸A. Kuppermann and Y. S. M. Wu, *Chem. Phys. Lett.* **205**, 577 (1993).
- ⁹R. Baer, D. M. Charutz, R. Kosloff, and M. Baer, *J. Chem. Phys.* **105**, 9141 (1996).
- ¹⁰D. R. Yarkony, *Rev. Mod. Phys.* **68**, 985 (1996).
- ¹¹T. Pacher, L. S. Cederbaum, and H. Koppel, *Adv. Chem. Phys.* **84**, 293 (1993).
- ¹²M. Baer, *J. Phys. Chem. A* **104**, 3181 (2000).
- ¹³M. Baer and A. Alijah, *Chem. Phys. Lett.* **319**, 489 (2000).
- ¹⁴M. Baer, *Phys. Rep.* **358**, 75 (2002).
- ¹⁵M. Lein, T. Kreibich, E. K. U. Gross, and V. Engel, *Phys. Rev. A* **65**, 033403 (2002).
- ¹⁶R. Baer, *J. Chem. Phys.* **117**, 7405 (2002).
- ¹⁷C. N. Yang and R. Mills, *Phys. Rev.* **95**, 631 (1954).