

Modified Born-Oppenheimer basis for nonadiabatic coupling: Application to the vibronic spectrum of HD^+

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Nonadiabatic matrix elements, when computed using a Born-Oppenheimer (BO) basis, do not vanish asymptotically because the motion of the electrons with the nuclei at large internuclear separations is not taken into account. We apply a method suggested by Delos [Rev. Mod. Phys. **53**, 287 (1981)] to include the effect of electron translation factors in a quantum-mechanical framework, thus correcting the BO basis to incorporate proper boundary conditions. We calculate the nonadiabatic matrix elements for H_2^+ and its isotopic variants. We focus our calculations on HD^+ , for which experimental results exist, and calculate its vibronic spectrum. This is the first application of this method to calculate high precision spectroscopic information for molecular systems.
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I. INTRODUCTION

Many calculations in molecular quantum chemistry rely on the Born-Oppenheimer (BO) approximation, in which, due to the large ratio between the mass of the electron and nuclei, the motion of the electrons is calculated in the presence of nuclei that are fixed in space.^{1,2} Therefore, the electronic motion depends parametrically on the position of the nuclei, but not on their momenta. Such calculations are often performed using one potential energy surface—the electronic ground state surface. In cases where there is a large difference in energy between the ground state and the excited states, the BO approximation is often adequate. However, in many cases, today's experiments and calculations are reaching the point where the accuracy required does not justify the use of the BO approximation. Moreover, for processes involving excited electronic states, or where more than one potential energy surface correlates to the same asymptotic limit, and particularly in the vicinity of curve-crossing, the BO approximation can become a poor approximation. One way to go beyond the BO approximation is to include nonadiabatic correction terms by expanding the total wave function in an adiabatic representation using a BO basis (BOBS). In this way, the interaction between the electronic degrees of freedom and the nuclear degrees of freedom is taken into account, and higher accuracy can be attained. This method is sometimes referred to as perturbed stationary states (PSS) theory.³

One of the few molecular systems where an exact quantum-mechanical calculation of the BO wave function can be performed is the one-electron system, H_2^+ , and its isotopic variants. The electronic wave function can be solved exactly, since the electronic Hamiltonian is separable upon transforming to prolate spheroidal coordinates. Hence, one can calculate the nonadiabatic corrections exactly, estimate their contribution to bound-state energies, and determine collisional information (e.g., cross sections). This system is ideal for testing the BO approximation, and also for testing

the use of the BO basis in calculations involving nonadiabatic corrections to structure and dynamics. However, an attempt to use a simple expansion of the total wave function in terms of BO states leads to serious problems.⁴⁻⁶ This is because the BO wave functions do not account for the motion of the electron with one of the nuclei at large internuclear separation. It results in nonadiabatic coupling matrix elements which do not vanish asymptotically. Therefore a scattering theory can not be developed, and bound-state properties are incorrectly determined. In classical and semiclassical theories of molecular dynamics, this electronic motion is incorporated by introducing “electron translation factors” (ETFs) which multiply the BO wave functions, and describe the change in momentum and kinetic energy of the electrons as they ride on the nuclei at large internuclear separation.⁷⁻¹¹ Incorporation of the effect of the asymptotic motion of electrons with the nuclei in a quantum-mechanical theory is necessary in order to describe structure and dynamics correctly. To date, calculations using these concepts have only been worked out in the context of collision dynamics⁴ and have not been tested in the regime of high precision spectroscopy where stringent comparison with high quality data can be made.

Other methods exist that can be used to calculate vibronic energies of H_2^+ without taking ETFs into account. Among them is the variational method of Bishop,^{12,13} which uses analytic functions as a basis set. This method is accurate only when low lying bound states are involved. The method of Wolniewicz and Poll^{14,15} is based on perturbation theory, but can not be used for excited states. Moss has significantly improved the accuracy of the calculations by using the transformed Hamiltonian method,¹⁶ and the artificial channel method of Balint-Kurti *et al.*¹⁷ However, although the results of Moss for the transition frequencies of the ground state of HD^+ are the most accurate to date, this method is also limited when bound-state energies of the excited states are involved. Furthermore, this method does not produce a wave function. The reviews by Carrington *et al.*¹⁸ and Leach and Moss¹⁹ summarize the advantages and disadvantages of these methods. An adiabatic hyperspherical treatment was

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suggested by Soloviev²⁰ and Macek.^{21,22} Hyperspherical coordinates have been shown to be a natural system of coordinates to describe molecular problems and yet incorporate the asymptotic motion of the electrons with the nuclei. However, since the resulting differential equations are complicated, it has been used primarily within the adiabatic approximation. Moreover, the overwhelming majority of molecular structure calculations are carried out using an adiabatic BO approach, and a tremendous investment into computer codes exists using these methods. Hence, it is important to determine the corrections necessary to the BO basis in order to incorporate the electronic motion with the nuclei asymptotically, and characterize the results obtained with these corrections by comparing the results with high precision spectroscopic data.

A theory for including the motion of electrons with the nuclei was developed by Delos, Thorson and others.^{4,7,23} A related method has been suggested by Green.²⁴ The basic idea behind these methods is the use of a generalized scattering coordinate which is a function of both the nuclear coordinate and the electronic coordinate in a quantum-mechanical framework. To the best of our knowledge, such methods were never applied to calculate high accuracy bound-state energies of the hydrogen molecular ion nor any other spectroscopic data for other molecular systems.

In this paper, we have modified the approach of Delos⁴ to formulate a theory that can be applied to calculate bound-state energies of both the ground and excited states of the molecular hydrogen ion. Here we present our results for HD^+ and compare with experimentally determined transition energies. The adiabatic BOBS theory of the three-body problem is reviewed in Sec. II. In Sec. III, the modified BOBS theory (MBOBS) is presented. Results and discussion are presented in Sec. V, and conclusions are drawn in Sec. VI.

II. BORN-OPPENHEIMER BASIS FORMULATION OF THE THREE-BODY PROBLEM

A. Statement of the problem

Consider the system described in Fig. 1. Here A and B are nuclei with mass M_A and M_B (in what follows we assume $M_A \geq M_B$), and \vec{R} is the nuclear coordinate going from A to B . The electronic coordinate can be chosen as \vec{r}_g , which connects the geometric center of the nuclei with the electron, or \vec{r} , which connects the center of mass of the two nuclei with the electron. The vectors \vec{R} , \vec{r} and \vec{r}_g are related via the expression

$$\vec{r}_g = \vec{r} - \frac{\lambda}{2} \vec{R}. \quad (1)$$

Here $\lambda = (M_A - M_B)/(M_A + M_B)$ is the mass asymmetry factor (note that $0 \leq \lambda < 1$ since $M_A \geq M_B$).²⁵ Accordingly, the gradient with respect to the nuclear coordinate \vec{R} is related using Eq. (1),

$$\vec{\nabla}_R |_{\vec{r}} = \vec{\nabla}_R |_{\vec{r}_g} - \frac{\lambda}{2} \vec{\nabla}_g \Big|_{\vec{R}}, \quad (2)$$

where $\vec{\nabla}_g$ means a gradient with respect to \vec{r}_g holding \vec{R} fixed. For simplicity of notation, we define

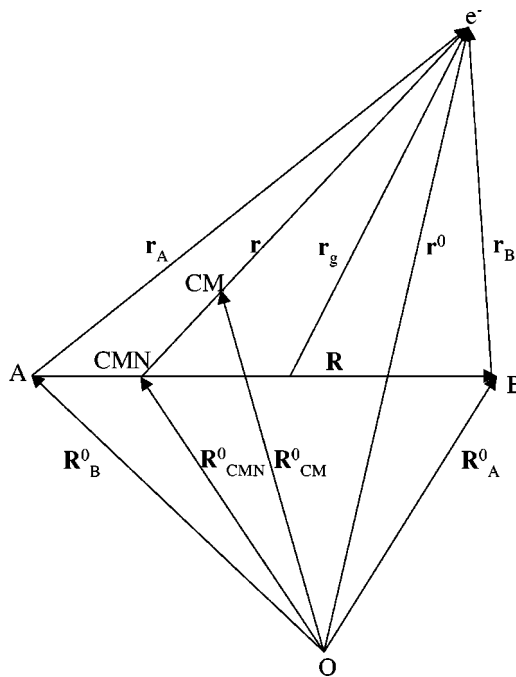


FIG. 1. Coordinates for the one-electron-two nuclei system. O is an external origin. CMN is the center of mass of the two nuclei A and B . CM is the center of mass of the whole system. \vec{r}_g is a vector from the geometric center of the nuclei to the electron. It is assumed that $M_A > M_B$.

$$\vec{\nabla}_R \equiv \vec{\nabla}_R |_{\vec{r}_g}. \quad (3)$$

The total Hamiltonian for the two nuclei and one electron, after subtracting off the center of mass contribution, can be written in atomic units as

$$H = -\frac{1}{2m} \nabla_g^2 - \frac{1}{2\mu} \left(\vec{\nabla}_R - \frac{\lambda}{2} \vec{\nabla}_g \right)^2 + \frac{1}{R} - \frac{1}{r_A} - \frac{1}{r_B}. \quad (4)$$

The masses are defined by

$$\begin{cases} \mu = \frac{M_A M_B}{M_A + M_B} \\ \frac{1}{m} = \frac{1}{m_e} + \frac{1}{M_A + M_B} \end{cases},$$

where m_e is the mass of the electron, and r_i ($i=A, B$) is the distance between the nucleus i and the electron. The Schrödinger equation takes the form

$$H\Psi(\vec{r}_g, \vec{R}) = E\Psi(\vec{r}_g, \vec{R}), \quad (5)$$

and the wave function Ψ can be expanded in an adiabatic BO basis set of electronic wave functions,

$$\Psi(\vec{r}_g, \vec{R}) = \sum_k \varphi_k(\vec{r}_g, R) F_k(\vec{R}), \quad (6)$$

where $\{\varphi_k(\vec{r}_g, R)\}$ are the electronic wave functions and $\{F_k(\vec{R})\}$ are the nuclear wave functions.

The electronic Hamiltonian is given by

$$h = -\frac{1}{2m} \nabla_g^2 - \left[\frac{1}{r_A} + \frac{1}{r_B} \right] = T + V. \quad (7)$$

The set of adiabatic BO functions $\{\varphi_k(\vec{r}_g, R)\}$ are eigenfunctions of the electronic Hamiltonian, and obey the eigenvalue equation

$$h\varphi_k(\vec{r}_g, R) = \varepsilon_k(R)\varphi_k(\vec{r}_g, R). \quad (8)$$

Inserting Eq. (6) into the Schrodinger equation, multiplying on the left by an electronic function and integrating over all electronic coordinates, results in a set of coupled differential equations for the nuclear wave function $F(\vec{R})$,

$$\left\{ -\frac{1}{2\mu}[\mathbf{1}\nabla_R^2 + 2\vec{\mathbf{P}}(R) \cdot \vec{\nabla}_R + \mathbf{B}^0(R)] + \mathbf{U}(R) \right\} \mathbf{F}(\vec{R}) = E\mathbf{F}(\vec{R}). \quad (9)$$

Here $\vec{\mathbf{P}}$ and \mathbf{B}^0 are the first and second derivative coupling matrices given by

$$\vec{P}_{k'k}(R) = \int d\vec{r}_g \varphi_{k'}(\vec{r}_g, R) \left(\vec{\nabla}_R - \frac{\lambda}{2} \vec{\nabla}_g \right) \varphi_k(\vec{r}_g, R) \quad (10)$$

and

$$B_{k'k}^0(R) = \int d\vec{r}_g \varphi_{k'}(\vec{r}_g, R) \left(\vec{\nabla}_R - \frac{\lambda}{2} \vec{\nabla}_g \right)^2 \varphi_k(\vec{r}_g, R). \quad (11)$$

The potential energy matrix \mathbf{U} is given by: $U_{k'k}(R) = (\varepsilon_k(R) + (1/R))\delta_{k'k}$. The solution of Eq. (9) is performed in two steps. First, Eq. (8) is solved to get the basis set functions $\{\varphi_k\}$ and the potential energies ε_k as a function of internuclear coordinate. This is done by transforming the problem into prolate spheroidal coordinates in which the electronic Hamiltonian is separable.²⁶ In the second step, Eq. (9) is converted to a radial equation by transformation to a rotating coordinate system, and expansion of the wave function in symmetric-top eigenfunctions followed by integration over the angular coordinates, as explained, e.g., in Refs. 27 and 28. The resulting nuclear wave function $\mathbf{G}(R)$ is a function of the magnitude of the nuclear coordinate only. The radial equation is then solved to obtain the bound-state energies and the wave function. For more details see Appendix A.

The differential equation for the nuclear wave function $\mathbf{G}_{M_J}^J$ and the eigenenergy E is given by

$$-\frac{1}{2\mu} \left[\mathbf{1} \left(\frac{d^2}{dR^2} - \frac{J(J+1) - 2\Lambda^2}{R^2} \right) + 2\mathbf{P}^{(R)} \frac{d}{dR} + \mathbf{B}^0 + \mathbf{D}^0 \right] \mathbf{G}_{M_J}^J = (E - \mathbf{U}) \mathbf{G}_{M_J}^J, \quad (12)$$

where $\mathbf{P}^{(R)}$ is the radial part of the first derivative coupling term $\vec{\mathbf{P}}$, \mathbf{D}^0 is the coupling matrix originating from the angular terms of the nuclear kinetic energy operator $-\nabla_R^2/2\mu$ which are off-diagonal in the magnetic quantum number Λ , and the matrix \mathbf{B}^0 has been defined above. The sum of the nonadiabatic coupling terms appearing in Eq. (12) is Hermitian, although neither $\vec{\mathbf{P}}$ nor \mathbf{B}^0 are Hermitian. Equation (12) can be written in an explicitly Hermitian form as follows:

$$-\frac{1}{2\mu} \left[\mathbf{1} \left(\frac{d^2}{dR^2} - \frac{J(J+1) - 2\Lambda^2}{R^2} \right) + \mathbf{P}^{(R)} \frac{d}{dR} + \frac{d}{dR} \mathbf{P}^{(R)} + \tilde{\mathbf{B}}^0 + \mathbf{D}^0 \right] \mathbf{G}_{M_J}^J = [E - \mathbf{U}] \mathbf{G}_{M_J}^J. \quad (13)$$

Here $\tilde{\mathbf{B}}^0$ is the Hermitian matrix,

$$\tilde{\mathbf{B}}^0 = \mathbf{B}^0 - \left(\frac{d}{dR} \mathbf{P}^{(R)} \right). \quad (14)$$

The derivative with respect to R in the second term on the right-hand side of Eq. (14) operates only on $\mathbf{P}^{(R)}$ and no further. For more details, see Appendix A.

B. Problems associated with the Born-Oppenheimer basis set

The main problem with the BOBS theory when applied to the molecular hydrogen ion is that individual terms in the expansion [Eq. (6)] do not satisfy the scattering boundary conditions.^{4,5} Since the sum over states is truncated in practice, the result is that the total wave function does not obey standard scattering boundary conditions as well. Asymptotically, the picture changes from a molecular picture to an atomic picture wherein the electron moves with one of the nuclei. However, the BO basis set functions are molecular in nature. They are therefore unable to describe the correct physics asymptotically. As a consequence, several difficulties appear which are evident upon calculations of the matrix elements of the first derivative coupling matrix $\vec{\mathbf{P}}$.

- (1) *The first derivative coupling matrix $\vec{\mathbf{P}}$, does not vanish asymptotically as $R \rightarrow \infty$.* This is because in the calculation of matrix elements of $\vec{\nabla}_R$, the electronic coordinate is held fixed with respect to the geometric center of the nuclei rather than with respect to either nucleus. A calculation of these terms shows that as $R \rightarrow \infty$, $\vec{P}_{k'k}(R) \rightarrow \text{const}$ which is not necessarily zero. Physically, this represents the motion of the atomic orbitals relative to the center of mass of the nuclei as R changes. These findings do not allow a scattering theory to be formulated, since boundary conditions are not obeyed.
- (2) *The first derivative coupling term $\vec{\mathbf{P}}$ also contains fictitious "origin dependent" couplings.* This is evident when one calculates the $\vec{\mathbf{P}}$ matrix between states with different parity (g, u) and are again a result of the inappropriate formulation of the theory. This is particularly important in the ground state manifold of HD^+ , where the only contribution to the matrix $\vec{\mathbf{P}}$ is fictitious. Calculations of the $\vec{\mathbf{P}}$ matrix show a non-negligible contribution between the states $1s\sigma_g$ and $2p\sigma_u$, whose order of magnitude is much too large. These contributions are eliminated in the corrected theory described below.

The common source of the above problems is the lack of a proper formulation of the asymptotic coupling between the electronic motion and the nuclei motion within the quantum theory. Semiclassically, this coupling is represented by electron translation factors (ETFs). An ETF on nucleus A is described by⁴

$$F_A(\vec{r}, t) = \exp \left[\frac{i}{\hbar} (m \vec{v}_A \cdot \vec{r} - \frac{1}{2} m v_A^2 t) \right], \quad (15)$$

where \vec{v}_A is the velocity of nucleus A , and \vec{r} is the electronic coordinate. The ETF represents the momentum and kinetic

energy of the electron as it rides on nucleus A or B . The electronic wave function for the electron around nucleus A can be defined as

$$\psi_{k,A}(\vec{r},t) = F_A(\vec{r},t) \varphi_{k,A}(\vec{r}_A) \exp\left[-\frac{i}{\hbar} \epsilon_{k,A} t\right]. \quad (16)$$

Here $\varphi_{k,A}(\vec{r}_A)$ is an ordinary atomic orbital for atom A , and $\epsilon_{k,A}$ is its energy. To elaborate on this point, we note that the coupling matrix $\vec{\mathbf{P}}$ represents the total change of the basis functions with respect to the nuclear coordinate R . The effect of the coupling matrix $\vec{\mathbf{P}}$ can be divided into two parts,

- (1) Rotation, distortion, polarization and change of character of the basis set functions with R .
- (2) Motion of the electron along with the atomic nuclei.

The first part is responsible for nonadiabatic transitions. Couplings originating from the second part are not physical, as was shown by Delos.⁴ Including the effect of ETFs in a quantum theory cancels the fictitious couplings that would otherwise be present. However, quantum mechanically, it is not clear how to define ETFs since they involve the velocity of one of the nuclei, and thus become ambiguous in the molecular adiabatic BO basis. Steps to overcome this problem have been taken by Thorson and Delos⁷ and Davis and Thorson.²³ Delos⁴ generalized those methods to the quantum case and developed a theory in which the effect of the asymptotic motion of the electrons with the nuclei is included in a quantum-mechanical fashion. The main idea of his method is a generalized scattering coordinate which is a function of both the nuclear coordinate and the electronic coordinate. In this theory, called the modified Born-Oppenheimer basis set (MBOB) method, all of the problems listed above are eliminated. The generalized scattering coordinate is constructed using a switching function that describes an electron translation which is a function of the electron's local behavior. As a consequence, the scattering coordinate switches between the nuclear coordinate \vec{R} at short range and the atomic coordinate \vec{R}_i ($i=A,B$) at long range. Davis and Thorson tested their theory on resonant-near-resonant charge exchange collision problems.²³ However, application of these methods was not performed in the context of bound-state energies of the hydrogen molecular ion nor any other molecular system. The details of this method are described in the next section.

III. THE MODIFIED BORN-OPPENHEIMER BASIS SET FORMULATION

A. The basic ansatz

As described above, individual terms in the BOBS expansion for the total wave function do not satisfy standard scattering boundary conditions. The main reason is the fact that asymptotically, the electron is bound to one of the nuclei and thus, upon dissociation, the system is best described in terms of atomic coordinates. There are three different Jacobi sets of coordinates which can be used to describe the one-electron two-nuclei system at different stages of the scattering process. These are illustrated in Fig. 2. A realistic scat-

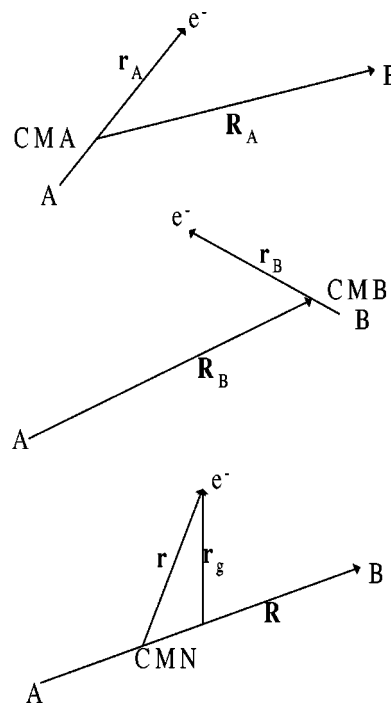


FIG. 2. Three Jacobi coordinate systems for relative coordinates of two heavy particles A , B , and an electron e^- for the case where $M_A > M_B$.

tering coordinate must be able to smoothly transform from the molecular picture with \vec{R} as the scattering coordinate to the atomic situation at dissociation described by \vec{R}_A or \vec{R}_B as the scattering coordinate (see Fig. 2). One should expect that the scattering coordinate will be a function of both the nuclear coordinate \vec{R} and the electronic coordinate \vec{r}_g . Following Delos,⁴ we thus define the scattering coordinate to be $\vec{\tilde{R}}(\vec{r}_g, \vec{R})$. In general, the coordinate \vec{R} can be state-dependent. A complete treatment with a state-dependent scattering coordinate can be found in Ref. 28. In the calculations we present here, we have taken \vec{R} as state-independent. The BOBS expansion of the total wave function is then replaced by the ansatz:

$$\Psi(\vec{r}_g, \vec{R}) = \sum_k \hat{\varphi}_k(\vec{r}_g, \vec{R}) F_k(\vec{\tilde{R}}). \quad (17)$$

If the basis set functions $\{\hat{\varphi}_k\}$ are of atomic character (i.e., single-center functions) then one may replace $\vec{\tilde{R}}$ by \vec{R}_A (\vec{R}_B) or a constant times \vec{R}_A (\vec{R}_B). But, if the basis set functions are of molecular character (two-center functions) then $\vec{\tilde{R}}$ becomes a curvilinear coordinate.

B. Derivation of the coupled equations

A complete derivation of the coupled equations resulting from Eq. (17) is presented in the review article by Delos.⁴ Here we survey the main results. The heavy-particle coordinate is chosen to be

$$\vec{\tilde{R}}(\vec{r}_g, \vec{R}) = \vec{R} + \frac{m}{\mu} \vec{s}(\vec{r}_g, \vec{R}), \quad (18)$$

where

$$\vec{s} = \frac{1}{2}(f+\lambda)\vec{r}_g - \frac{1}{8}(1-\lambda^2)\vec{R}. \quad (19)$$

$f=f(\vec{r}_g, R)$ is a switching function which is antisymmetric with respect to electronic coordinate \vec{r}_g , and goes asymptotically as $R \rightarrow \infty$ to ± 1 . Asymptotically, $\vec{R} \approx \sqrt{(\mu_i/\mu)}\vec{R}_i$ ($i=A, B$), μ_i being the nuclear reduced mass in channel i , e.g., $\mu_A = (m_e + M_A)M_B / (m_e + M_A + M_B)$. The main reason this particular choice of scattering coordinate is chosen comes from the fact that using this form in a classical theory has resolved many of the problems of the BOBS theory.⁴ However, the switching function is yet to be determined.

The next step is to map the original BO basis set $\{\varphi_k(\vec{r}_g, R)\}$ by using new coordinates so as to create the basis $\{\hat{\varphi}_k(\vec{r}_g, \vec{R})\}$. The final step is to express the Hamiltonian in Eq. (4) in terms of the new set of coordinates. As a result, the Hamiltonian can be expanded in powers of $\sqrt{m/\mu} \approx v_{\text{nuclear}}/v_{\text{electronic}}$. Since the collisions considered are slow, one can assume that the nuclear velocity is much smaller than the typical electronic velocity, so that terms of order $(m/\mu)^{3/2}$ ($\approx 10^{-5}$ for H_2^+) and higher powers can be consistently neglected. In addition, terms of order m/μ which are also proportional to derivatives of the switching function or related factors [e.g., (f^2-1)] can also be neglected. The matrix elements of the new Hamiltonian are given by (the coordinate \vec{r} , rather than \vec{r}_g is used for the sake of consistency with Ref. 4; the transformation between the two coordinates is performed later on),

$$\begin{aligned} \langle \Psi | H(\vec{r}, \vec{R}) | \Psi \rangle \\ = \sum_{k', k} \langle \hat{\varphi}_{k'}(\vec{r}, \vec{R}) F_{k'}(\vec{R}) | h' | \hat{\varphi}_k(\vec{r}, \vec{R}) F_k(\vec{R}) \rangle \\ - \frac{1}{2\mu} \sum_{k', k} [\langle \hat{\varphi}_{k'}(\vec{r}, \vec{R}) F_{k'}(\vec{R}) | D^a D^a | \hat{\varphi}_k(\vec{r}, \vec{R}) F_k(\vec{R}) \rangle \\ + \langle \hat{\varphi}_{k'}(\vec{r}, \vec{R}) F_{k'}(\vec{R}) | \partial \alpha^{ab} / \partial r^a D^a | \hat{\varphi}_k(\vec{r}, \vec{R}) F_k(\vec{R}) \rangle], \end{aligned} \quad (20)$$

with

$$h' = -\frac{1}{2m} \left[p^a p^a - \frac{m}{\mu} \alpha^{ba} \alpha^{ca} p^b p^c \right] + V + \frac{1}{R}, \quad (21)$$

and $D^a = P^a + \alpha^{ba} p^b$, where a, b represent the directions $\hat{i}, \hat{j}, \hat{k}$ and the summation over common indices is implicit. Here we used the definitions

$$p^b = (\partial / \partial r^b)_{\vec{r}}; \quad P^b = (\partial / \partial \vec{R}^b)_{\vec{r}}; \quad \alpha^{ab} = (\partial s^b / \partial r^a)_{\vec{r}}. \quad (22)$$

Note that \vec{P} is a derivative with respect to \vec{R} holding \vec{r} fixed, not \vec{r}_g , so care must be taken before comparison with the results of the BOBS method (in which all derivatives with respect to the scattering coordinate were derived holding \vec{r}_g fixed) can be performed.

For the purpose of numerical integration over electronic coordinates, \vec{R} is a dummy integration variable. We can

therefore designate it by the numerical value R . Using the Hamiltonian given in Eq. (20), a new set of coupled equations results,

$$\left\{ -\frac{1}{2\mu} [\mathbf{1}\nabla_R^2 + 2\vec{\Pi} \cdot \vec{\nabla}_R + \mathbf{B}] + \mathbf{U} + \mathbf{I} - \mathbf{1}E \right\} \mathbf{F}(\vec{R}) = 0, \quad (23)$$

where \mathbf{U} is as before, and the coupling matrices are given by

$$\begin{cases} \Pi_{k'k} = \int d\vec{r}_g \hat{\varphi}_{k'} \left(D^a + \frac{1}{2} \frac{\partial \alpha^{ba}}{\partial r^b} \right) \hat{\varphi}_k, \\ B_{k'k} = \int d\vec{r}_g \hat{\varphi}_{k'} D^a D^a \hat{\varphi}_k, \\ I_{k'k} = \int d\vec{r}_g \hat{\varphi}_{k'} \left[h' - \hat{h} - \frac{1}{R} \right] \hat{\varphi}_k. \end{cases} \quad (24)$$

C. Interpretation of coupling terms

1. The potential energy matrix \mathbf{U}

The potential energy matrix $\mathbf{U}(R)$ is given by matrix elements of the operator h plus the factor of $1/R$ exactly as in the BOBS theory. The electronic Hamiltonian that should be used to define the potential energy matrix in Eq. (23) is h' , which is the operator defined in Eq. (21). However, it is convenient to express h' in the form

$$h' = \hat{h} + \frac{1}{R} + \left(h' - \hat{h} - \frac{1}{R} \right) = \hat{h} + \frac{1}{R} + I. \quad (25)$$

The electron reduced mass matrix \mathbf{I} defined by the above equation will be discussed below. The electronic Hamiltonian operator \hat{h} bears the same relationship to the BO electronic Hamiltonian h that $\hat{\varphi}_k(\vec{r}, \vec{R})$ bears to $\varphi_k(\vec{r}, R)$. Expressed in terms of (\vec{r}, \vec{R}) , \hat{h} has the same functional form as does h expressed in terms of (\vec{r}, R) . In other words, \hat{h} can be thought of as a ‘‘mapping’’ of the BO electronic Hamiltonian to the new coordinates. We thus have

$$\begin{aligned} U_{k'k} &= \int d\vec{r} \hat{\varphi}_{k'}(\vec{r}, \vec{R}) \left(\hat{h} + \frac{1}{R} \right) \hat{\varphi}_k(\vec{r}, \vec{R}) \\ &= \int d\vec{r}_g \varphi_{k'}(\vec{r}_g, R) \left(h + \frac{1}{R} \right) \varphi_k(\vec{r}_g, R) \\ &= \left(\varepsilon_k + \frac{1}{R} \right) \delta_{k'k}. \end{aligned} \quad (26)$$

The last equality is obtained provided the basis set functions are eigenstates of the electronic Hamiltonian. Moreover, the electronic wave functions are orthogonal, i.e.,

$$\begin{aligned} S_{k'k} &= \int d\vec{r} \hat{\varphi}_{k'}(\vec{r}, \vec{R}) \hat{\varphi}_k(\vec{r}, \vec{R}) \\ &= \int d\vec{r}_g \varphi_{k'}(\vec{r}_g, R) \varphi_k(\vec{r}_g, R) = \delta_{k'k}. \end{aligned} \quad (27)$$

Since the new electronic Hamiltonian \hat{h} is practically equal to the BO electronic Hamiltonian, the caret is omitted in Eq. (23) and in what follows.

2. The corrected first derivative coupling matrix $\tilde{\Pi}$

$$\begin{aligned}\tilde{\Pi}_{k'k} &= \int d\vec{r} \hat{\phi}_{k'}(\vec{r}, \vec{R}) \left(P^a + \alpha^{ba} p^b + \frac{1}{2} \frac{\partial \alpha^{ba}}{\partial r^b} \right) \hat{\phi}_k(\vec{r}, \vec{R}) \\ &= \int d\vec{r}_g \varphi_{k'}(\vec{r}_g, R) \left[\vec{\nabla}_R - \frac{\lambda}{2} \vec{\nabla}_g \right] \varphi_k(\vec{r}_g, R) \\ &\quad - m \int d\vec{r}_g \varphi_{k'}(\vec{r}_g, R) [\hat{h}, \vec{s}] \varphi_k(\vec{r}_g, R) \\ &= \tilde{P}_{k'k} + \tilde{A}_{k'k}.\end{aligned}\quad (28)$$

The first term (\tilde{P}) is the original first derivative coupling matrix appearing in the BOBS theory. The second term (\tilde{A}) is the correction matrix which cancels the fictitious couplings originating from the first derivative coupling matrix \tilde{P} . With $\tilde{\Pi}$ playing the role the matrix \tilde{P} plays in the BOBS theory, standard scattering boundary conditions are obtained. In the case of the state-dependent scattering coordinate, another matrix called $\tilde{\gamma}$ must be added to $\tilde{\Pi}$.^{4,28} This matrix originates from momentum transfer factors. However, when the scattering coordinate is state-independent, this matrix vanishes identically.

3. The corrected second derivative coupling matrix B

Using the definition in Eq. (24), we have

$$\begin{aligned}B_{k'k} &= \int d\vec{r} \hat{\phi}_{k'}(\vec{r}, \vec{R}) (P^a + \alpha^{ba} p^b)^2 \hat{\phi}_k(\vec{r}, \vec{R}) \\ &\approx \int d\vec{r}_g \varphi_{k'}(\vec{r}_g, R) \left[\vec{\nabla}_R + \frac{f}{2} \vec{\nabla}_g \right]^2 \varphi_k(\vec{r}_g, R).\end{aligned}\quad (29)$$

The last line of Eq. (29) is an approximation, since derivatives of the switching function f have been neglected. This approximation is fully justified asymptotically, since the switching function goes to a constant there. This approximation simplifies the calculations significantly.

4. The electron reduced mass matrix, I

The matrix I contains corrections related to the reduced mass of the electron. In the molecular BO basis set description, the reduced electronic mass taken into account [$m = m_e(M_A + M_B)/(m_e + M_A + M_B)$] is different from the atomic reduced electronic mass appearing in the channels: $m_i = m_e M_i/(m_e + M_i)$, $i = A, B$. The matrix I is proportional to the difference between these reduced masses. In other words, since the new first and second derivative coupling terms are made to vanish asymptotically, the remaining coupling terms originating from small mass differences need to be taken into account separately. This is the source of the I matrix which takes the form

$$\begin{aligned}I_{k'k} &= \int d\vec{r} \hat{\phi}_{k'}(\vec{r}, \vec{R}) \left[h' - \hat{h} - \frac{1}{\vec{R}} \right] \hat{\phi}_k(\vec{r}, \vec{R}) \\ &\approx \frac{1}{2\mu} \int d\vec{r}_g \varphi_{k'}(\vec{r}_g, R) [(f + \lambda) \nabla_g^2] \varphi_k(\vec{r}_g, R) \\ &\quad - \frac{m}{\mu} \int d\vec{r}_g \varphi_{k'}(\vec{r}_g, R) \vec{s} \cdot \vec{\nabla}_R \left(V + \frac{1}{R} \right) \varphi_k(\vec{r}_g, R).\end{aligned}\quad (30)$$

Here the last line results from the difference between the potential energy written in terms of (\vec{r}_g, R) and in terms of (\vec{r}_g, \vec{R}) .

Equation (23) involves three nuclear dimensions. It can be reduced to a one dimensional radial equation in a fashion similar to that used in the original BOBS theory — by expansion in symmetric-top eigenfunctions.

D. The radial equation

In deriving the radial equation, the same expansion as in the BOBS theory [Eq. (A2)] was used. Clearly, the same symmetry restrictions regarding the magnetic quantum number Λ appear here as well. The resulting equation is very similar to Eq. (12) except for the addition of the matrix I , and is given by

$$\begin{aligned}E \mathbf{1} \mathbf{G}_{M_J}^J &= -\frac{1}{2\mu} \mathbf{1} \left(\frac{d^2}{dR^2} - \frac{J(J+1) - 2\Lambda^2}{R^2} \right) \mathbf{G}_{M_J}^J \\ &\quad - \frac{1}{2\mu} \left[2\mathbf{\Pi}^{(R)} \frac{d}{dR} + \mathbf{B} + \mathbf{D} - 2\mu(\mathbf{I} + \mathbf{h}) \right] \mathbf{G}_{M_J}^J.\end{aligned}\quad (31)$$

Here $\mathbf{\Pi}^{(R)}$ means the radial part of the matrix $\tilde{\Pi}$, \mathbf{B} is diagonal in Λ , \mathbf{D} is a matrix representing the off-diagonal in Λ coupling terms originating from the angular part of the matrix $\tilde{\Pi}$ and the angular part of the nuclear kinetic energy operator $-\nabla_g^2/2\mu$. All of these matrix elements are specified in detail in Appendix B.

E. Hermitian formulas for the matrix elements

The issue of hermiticity requires special attention since the discrete variable representation (DVR) method (used to find the eigenenergies and eigenfunctions of the nuclear Hamiltonian) can lead to significant numerical errors if the Hamiltonian matrix is not written in an explicitly Hermitian form.²⁹ Therefore, each coupling matrix should be examined carefully. Since all operators and basis set functions are real, one should require that the nuclear Hamiltonian will be symmetric with respect to interchanging basis set indices.

We start by writing the radial Eq. (31) as follows:

$$\begin{aligned}E \mathbf{1} \mathbf{G}_{M_J}^J &= -\frac{1}{2\mu} \mathbf{1} \left(\frac{d^2}{dR^2} - \frac{1}{R^2} (J(J+1) - 2\Lambda^2) \right) \mathbf{G}_{M_J}^J \\ &\quad - \frac{1}{2\mu} \left(\mathbf{\Pi}^{(R)} \frac{d}{dR} + \frac{d}{dR} \mathbf{\Pi}^{(R)} \right. \\ &\quad \left. + \tilde{\mathbf{B}} + \mathbf{D} - 2\mu(\mathbf{I} + \mathbf{h}) \right) \mathbf{G}_{M_J}^J.\end{aligned}\quad (32)$$

Here $\tilde{\mathbf{B}} = \mathbf{B} - ((d/dR)\mathbf{\Pi}^{(R)})$, where the derivative operates on $\mathbf{\Pi}^{(R)}$ only.

The radial part of the first derivative coupling matrix $\tilde{\Pi}$ must be antisymmetric because it multiplies the operator d/dR which is antisymmetric. From Eq. (B1) one can easily see that this is indeed the case.

The second derivative matrix \mathbf{B} need not be Hermitian in general. Nevertheless, in analogy with the BOBS theory, we expect to find the matrix $\tilde{\mathbf{B}}$ Hermitian. The expression given

in Appendix B proves this assumption. In practice, however, a derivation of a formula for $(-(1/2\mu)\tilde{\mathbf{B}}+\mathbf{I})$ is simpler than deriving $\tilde{\mathbf{B}}$ and \mathbf{I} separately.²³ The resulting formula is Hermitian per definition, and is given by (see Appendix C for details)

$$\begin{aligned} & -\frac{1}{2\mu}\tilde{\mathbf{B}}_{k'k}+I_{k'k} \\ & = -\frac{1}{2\mu}\tilde{\mathbf{B}}_{k'k}^0 - \frac{m}{2\mu}\left(\varepsilon'_{k'}+\varepsilon'_k-\frac{2}{R^2}\right)s_{k'k}^{(R)} \\ & \quad - \frac{m}{2\mu}(\varepsilon_k-\varepsilon_{k'})\langle k'\Lambda|\vec{s}\cdot\left(\vec{\nabla}_R-\frac{1}{2}\lambda\vec{\nabla}_g\right)|k\Lambda\rangle \\ & \quad - \frac{m}{2\mu}(\varepsilon_k-\varepsilon_{k'})\langle k'\Lambda|\left(\vec{\nabla}_R-\frac{1}{2}\lambda\vec{\nabla}_g\right)\cdot\vec{s}|k\Lambda\rangle. \end{aligned} \quad (33)$$

Here again, integration is over the prolate spheroidal coordinates, ξ , η and χ . Within the $1s\sigma_g$ and $2p\sigma_u$ manifold of H_2^+ states (states are designated by the united atom limit quantum numbers), the off-diagonal elements of the second term on the right-hand side of Eq. (33) vanish because of symmetry. This is because the radial part of the vector \mathbf{s} is symmetric with respect to the prolate electronic coordinate η , while the electronic wave functions of $1s\sigma_g$ and $2p\sigma_u$ are symmetric and antisymmetric with respect to η , respectively. Therefore the integrand is antisymmetric, while the integration boundaries are symmetric and the integral vanishes. The third and fourth terms on the right-hand side of Eq. (33) vanish asymptotically since the energies of the ground state manifold are degenerate asymptotically. In the ground state manifold of HD^+ it is therefore possible to estimate the off-diagonal elements of the matrix $[-(1/2\mu)\tilde{\mathbf{B}}_{k'k}+I_{k'k}]$ assuming $\varepsilon_k\approx\varepsilon_{k'}$ at any point in R . The result is the BOBS Hermitian second derivative term $-(1/2\mu)\tilde{\mathbf{B}}_{k'k}^0$.

The matrix \mathbf{D} as defined by Eq. (B7) is also Hermitian, since the original BOBS \mathbf{D}^0 matrix is Hermitian.

To summarize, as in the BOBS theory, we are able to formulate the radial Schrodinger equation in an explicitly Hermitian form. It should be noted that using a state-dependent scattering coordinate (by means of a state-dependent switching function), hermiticity of the resulting coupling matrices and the total Hamiltonian can not be assured.²⁸

IV. NUMERICAL CALCULATIONS OF VIBRONIC ENERGIES

The MBOBS method was used to calculate vibration-rotation energies of the hydrogen molecular ion and its isotopic variants (H_2^+ , HD^+ , D_2^+). The calculations were carried out in several steps:

(1) Solving the electronic wave equation for the electronic eigenenergies and the electronic wave functions. The eigenenergies are used to construct the potential energy curves for the nuclear problem, and the electronic wave functions are used as a basis set with which one expands the total wave function as in Eq. (17).

- (2) Calculating the coupling matrix elements necessary to construct the Hamiltonian matrix of the Hermitian nuclear radial equation [Eq. (32)].
- (3) Solving the nuclear radial eigenstate problem, Eq. (32), by means of a specially designed discrete variable representation (DVR) method.

The methods used for the calculations are described below.

A. Computational methods

1. Solution of the electronic problem

The electronic wave equation is given by

$$\begin{aligned} h\varphi(\vec{r}_g, R) & = \left[-\frac{\hbar^2}{2m}\nabla_g^2 - \frac{1}{|\vec{r}_A|} - \frac{1}{|\vec{r}_B|} \right] \varphi(\vec{r}_g, R) \\ & = \varepsilon(R)\varphi(\vec{r}_g, R). \end{aligned} \quad (34)$$

In prolate spheroidal coordinates this equation is separable, obtaining³⁰:

$$\begin{aligned} & \left[\frac{\partial^2}{\partial\chi^2} + \Lambda^2 \right] Z(\chi) = 0, \\ & \left[\frac{\partial}{\partial\xi}(\xi^2-1)\frac{\partial}{\partial\xi} + A - \frac{\Lambda^2}{\xi^2-1} + 2R\xi - p^2\xi^2 \right] X(\xi, R) = 0, \\ & \left[\frac{\partial}{\partial\eta}(1-\eta^2)\frac{\partial}{\partial\eta} - A - \frac{\Lambda^2}{1-\eta^2} + p^2\eta^2 \right] Y(\eta, R) = 0, \end{aligned} \quad (35)$$

where $p^2(R) = -(R^2/2)\varepsilon(R)$, and the electronic wave function takes the product form

$$\varphi(\vec{r}_g, R) = N(R)X(\xi, R)Y(\eta, R)Z(\chi). \quad (36)$$

Here $N(R)$ is the normalization constant such that

$$\frac{1}{2\pi} \int d\chi \int d\tau \varphi_{k'} \varphi_k = \delta_{k'k}, \quad (37)$$

with the volume element given by

$$d\tau = \frac{\pi R^3}{4}(\xi^2 - \eta^2)d\xi d\eta. \quad (38)$$

The solution of the first equation in (35) gives $Z(\chi) = \exp[i\Lambda\chi]$. Several methods have been developed through the years which can treat these kinds of differential equations in which the separation constant A and the energy constant p are R dependent, e.g., Refs. 26, 27, and 30–32. We used a computer program written by Hadinger and co-workers. This program is based on the Killingbeck method associated with Miller's algorithm.^{32–35} According to the method of Hadinger and co-workers, the functions $X(\xi, R)$ and $Y(\eta, R)$ are expanded in a suitable power series (there are several possibilities—see Ref. 32), obtaining recursion relations for the coefficients and solving them according to the Hill determinant method.³⁶ This method also allows accurate calculations of the first and second derivatives of the electronic wave function with respect to the nuclear coordinate. Hylleraas functions are used to expand the function $X(\xi, R)$,

$$\begin{aligned} X(\xi, R) & = (\xi^2 - 1)^{\Lambda/2} \exp[-p(\xi - 1)] \\ & \quad \times \sum_{j=0}^{\infty} C_j L_{\Lambda+j}^{\Lambda}(2p(\xi - 1)). \end{aligned} \quad (39)$$

The function $Y(\eta, R)$ is expanded using Baber and Hassè's functions,

$$Y(\eta, R) = \exp[-p\eta] \sum_{l=\Lambda} a_l P_l^\Lambda(\eta). \quad (40)$$

Here $P_l^\Lambda(\eta)$ are associated Legendre polynomials. Using this method we were able to obtain electronic wave functions and potential energy surfaces with accuracy of 11 to 15 significant digits.

In the next step, all the coupling matrix elements that appear in Eq. (32) were separated into integrals over ξ times integrals over η . The expansions of the electronic wave functions $X(\xi, R)$ and $Y(\eta, R)$ were used to calculate the various integrals semianalytically. For integrals involving the switching functions, the integration was performed numerically. When possible, the integrals were tested using identities specified in Ref. 28, and accuracy of 9 to 14 significant digits was obtained.

2. The choice of the switching function

The switching function was determined using the method of Thorson and co-workers.^{37,38} This method allows for both state-independent and state-dependent switching functions. In our calculations, we found implementation of the state-dependent switching function to be problematic,²⁸ hence we used the parameter $b(R)$ that was optimized for the ground state. An analytic function, $f(\eta, R) = \tanh[b(R)R\eta]$, was chosen for the switching function, where b is a function of the internuclear distance R . The switching function f is independent of ξ and χ . The specific choice of the parameter $b(R)$ was made by an optimization procedure that significantly reduced the magnitude of the corrected coupling matrices of the ground state to higher lying states as compared with the BOBS coupling matrices. $b(R)$ was determined empirically on a grid of points in R , and was then interpolated to obtain its value for any given R .

3. Diagonalization of the Hamiltonian

The radial equation resulting from the coupled equations [Eq. (32)] was solved using a Fourier grid Hamiltonian-discrete variable representation (FGH-DVR) method.³⁹⁻⁴¹ For the purpose of these calculations, the method was generalized to treat first derivative coupling terms. Furthermore, the method was formulated in a manner that is explicitly Hermitian and that does not involve products of operators that are difficult to evaluate analytically. The issue of hermiticity is crucial for these sort of calculations.²⁹ Ignoring this issue can result in significant numerical problems. A nonlinear grid in the scattering coordinate was used,⁴² in order to sample long range potentials with higher accuracy.

V. RESULTS AND DISCUSSION

A. Calculations of the coupling matrices

About 20 years ago, Ponomarev and co-workers published a series of papers on the use of BO basis functions to calculate nonadiabatic matrix elements of the three-body problem.⁴³⁻⁴⁵ In the third paper they presented figures of the

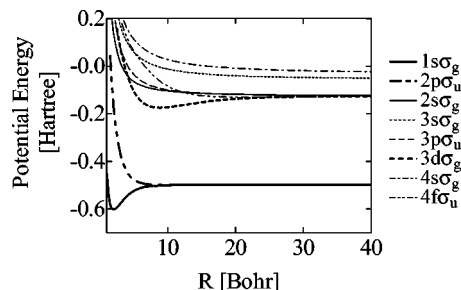


FIG. 3. Potential energy curves of H_2^+ and its isotopic variants for various σ states. United atom limit quantum numbers are used to designate states.

various matrix elements resulting from applying the BOBS theory. Their results, although correct mathematically, did not incorporate the correct physics associated with the motion of the electron with the nuclei asymptotically. A few years later, they performed some modifications to the BOBS theory;⁵ however, their generalized model did not solve all the problems arising from the BOBS theory, and was not applied to the calculations of bound-state energies of molecular hydrogen ion. Since then, various methods have been developed to calculate vibronic energies of the ground state of H_2^+ ,^{18,19} but none of these methods was used to determine correct nonadiabatic matrix elements. Moreover, some of these methods are based on transformations of the Hamiltonian such that the original meaning of the coupling matrices is lost.¹⁹ Therefore, it is important to determine these matrix elements and understand their behavior as a function of internuclear distance. Figure 3 presents the potential energy surfaces of H_2^+ and its isotopic variants, for states with quantum numbers $n=1\dots 4$, $\Lambda=0$. Figure 4 presents several matrix elements of the radial part of the first derivative matrix $\vec{\Pi}$ for HD^+ . One important thing to note here is that at large internuclear separation, all matrix elements vanish. Figure 5 presents the BOBS results [the radial part of the matrix \vec{P} , Eq. (A7)], for the same matrix elements presented in Fig. 4. In addition, Fig. 6 shows BOBS results of the radial part of the matrix \vec{P} , that couple gerade and ungerade states. These matrix elements vanish identically in the correct theory. Figure 7 presents few matrix elements of the radial parts of the matrices $\vec{\Pi}$ and \vec{P} . The main difference between the BOBS results and the MBOBS results is the asymptotic limit of the matrix elements, as is evident from Fig. 7. In addition, the matrix elements of $\Pi^{(R)}$ are smaller in magnitude as compared with the matrix elements of $P^{(R)}$. These

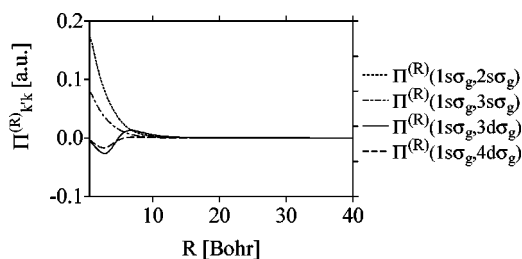


FIG. 4. Matrix elements of the MBOBS radial first derivative matrix calculated for HD^+ .

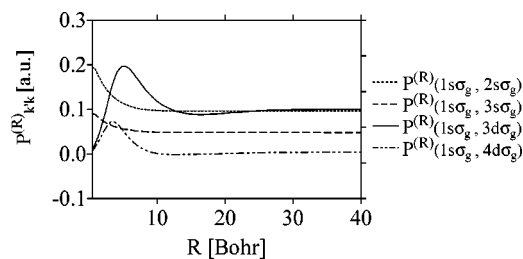


FIG. 5. Matrix elements of the BOBS radial first derivative matrix calculated for HD^+ .

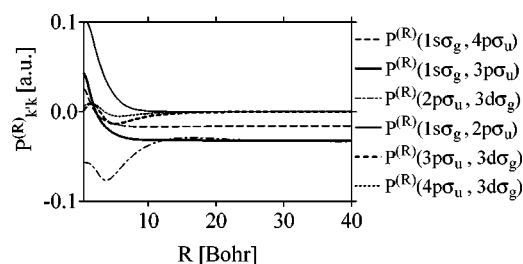


FIG. 6. Matrix elements of the BOBS radial first derivative matrix for HD^+ , for various gerade-ungerade states.

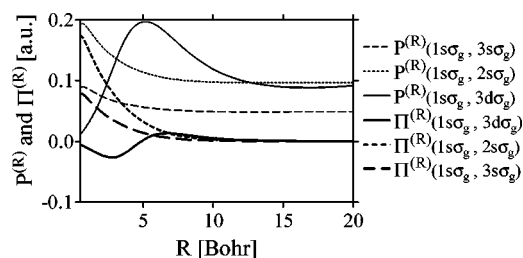


FIG. 7. Comparison between matrix elements of the BOBS radial first derivative matrix and the MBOBS radial first derivative matrix for HD^+ , for various σ_g states.

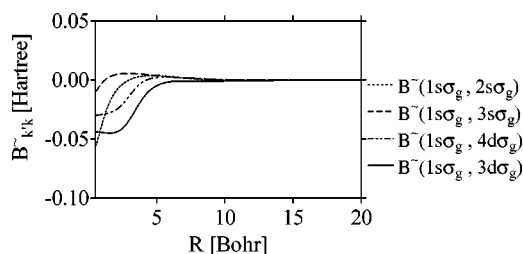


FIG. 8. Matrix elements of the MBOBS second derivative matrix calculated for HD^+ .

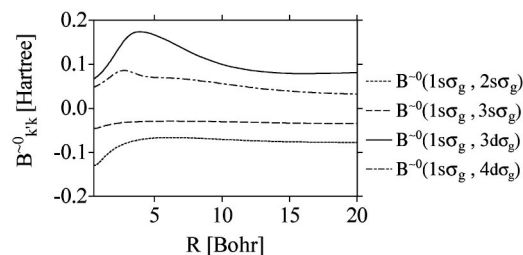


FIG. 9. Matrix elements of the BOBS second derivative matrix calculated for HD^+ .

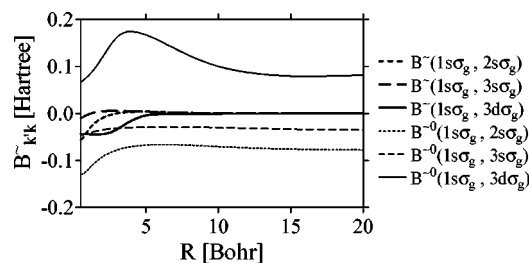


FIG. 10. Comparison between matrix elements of the BOBS second derivative matrix and the MBOBS second derivative matrix for HD^+ , for various σ_g states.

results suggest that convergence with respect to the basis set size can be much faster in the MBOBS method. Various matrix elements of the matrix $\tilde{\mathbf{B}}$ [Eq. (B5)] are plotted as a function of internuclear distance in Fig. 8. As expected, asymptotically, all matrix elements vanish. The result of the BOBS theory for the second derivative coupling matrix are presented in Fig. 9. A comparison with the second derivative matrix $\tilde{\mathbf{B}}^0$ of the BOBS theory [Eq. (A10)] is given in Fig. 10. Our calculations show that the coupling matrix elements of the matrices discussed above for states other than the ground state behave similarly, and are therefore not shown here.

Calculations of the off-diagonal elements of the electron reduced mass matrix \mathbf{I} are cumbersome, and require additional effort. The diagonal elements of the matrix \mathbf{I} are shown in Fig. 11.

B. Calculations of transition energies for HD^+

Of all isotopic equivalents of H_2^+ , HD^+ is the one which experimentalists study most.¹⁸ Hence, we focus our reported results on the HD^+ transition energies for which experimental measurements exist. Convergence as a function of the DVR parameters was examined. The integration region was $R \in [0.5, 100]$ Bohr, and 150 grid points were used with a nonlinear grid. With these parameters, the resulting bound states are believed to be accurate to at least nine significant digits. Table I presents results of Born-Oppenheimer, adiabatic and two-state nonadiabatic calculation of the transition frequencies of HD^+ and their comparison to experimental values. The BO results refer to the electronic Hamiltonian: $h^0 = -(1/2m_e)\nabla_g^2 + V$, where m_e , the electron mass, is taken as unity. The two-state nonadiabatic calculation was performed within the ground state manifold of HD^+ , meaning

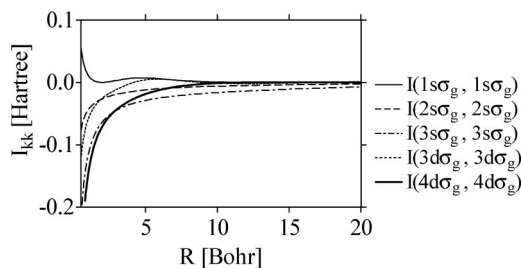


FIG. 11. Diagonal matrix elements of the reduced electronic mass matrix for HD^+ for various σ_g states.

TABLE I. BO, adiabatic, nonadiabatic two-state, radiatively and relativistically corrected nonadiabatic two-state and experimental transition frequencies of HD^+ in cm^{-1} . Percent difference refers to the difference between the radiatively and relativistically corrected two-state nonadiabatic calculations and experimental values. Experimental values are taken from Ref. 16.

Transition	BO	Adiabatic	Two-state	Corrected two-state	Experiment	% difference
1-0P(1)	1869.7222	1869.1685	1869.1683	1869.2044	1869.1340	0.0038
1-0P(2)	1824.1013	1823.5666	1823.5664	1823.5453	1823.5330	0.0007
1-0P(3)	1777.0063	1776.4916	1776.4914	1776.4717	1776.4590	0.0007
2-1R(0)	1857.3311	1856.8028	1856.8025	1856.7798	1856.7780	0.0001
3-2R(0)	1762.0999	1761.6312	1761.6309	1761.6106	1761.6160	0.0003
3-2R(1)	1798.0181	1797.5370	1797.5366	1797.5153	1797.5220	0.0004
3-2R(2)	1831.5890	1831.0970	1831.0967	1831.0744	1831.0830	0.0005
3-2P(2)	1642.5451	1642.1220	1642.1217	1642.1047	1642.1080	0.0002
17-14R(0)	1812.5097	1813.8616	1813.8194	1813.8401	1813.8520	0.0007
17-14R(1)	1818.8475	1820.2173	1820.1737	1820.1947	1820.2090	0.0008
17-14R(2)	1818.8154	1820.2107	1820.1651	1820.1865	1820.1990	0.0007
17-14R(3)	1812.2306	1813.6596	1813.6110	1813.6333	1813.6440	0.0006
17-14R(4)	1798.9062	1800.3775	1800.3249	1800.3484	1800.3580	0.0005
17-14R(5)	1778.6472	1780.1698	1780.1118	1780.1368	1780.1450	0.0005
17-14P(1)	1781.4424	1782.7810	1782.7397	1782.7606	1782.7720	0.0006
17-15R(7)	1077.6606	1078.8992	1078.8337	1078.8557	1078.8530	0.0003
17-15P(1)	1091.1578	1092.1390	1092.1051	1092.1212	1092.1240	0.0003
17-15P(2)	1070.5964	1071.5774	1071.5432	1071.5598	1071.5610	0.0001
17-15P(3)	1046.2704	1047.2562	1047.2211	1047.2382	1047.2390	0.0001
17-15P(5)	986.9302	987.9402	987.9014	987.9198	987.9170	0.0003
17-15P(6)	952.1780	953.2075	953.1657	953.1851	953.1800	0.0005
18-16R(0)	925.3510	926.5513	926.4805	926.5012	926.4900	0.0012
18-16R(1)	931.0682	932.2883	932.2141	932.2351	932.2240	0.0012
18-16R(2)	932.0357	933.2822	933.2027	933.2242	933.2130	0.0012
18-16R(3)	928.0434	929.3232	929.2362	929.2586	929.2470	0.0012
18-16R(4)	918.8643	920.1852	920.0873	920.1107	920.1000	0.0012
18-16R(5)	904.2475	905.6179	905.5046	905.5293	905.5190	0.0011
18-16R(6)	883.9049	885.3348	885.1985	885.2248	885.2180	0.0008
18-16P(1)	900.4452	901.6245	901.5558	901.5766	901.5650	0.0013
18-16P(2)	881.6168	882.7943	882.724	882.7454	882.7310	0.0016
19-16P(6)	1035.2059	1037.2543	983.6407	1036.9731	1036.9610	0.0012
19-16P(7)	981.9418	984.0473	1036.9335	983.6823	983.6930	0.0011
20-17R(0)	916.6325	918.9213	918.1018	918.1436	918.1020	0.0045
20-17R(1)	914.0502	916.3737	915.4529	915.4955	915.4760	0.0021
20-17R(2)	903.4980	905.8698	904.7563	904.8000	904.8330	0.0036
20-17R(3)	884.5929	887.0288	885.5384	885.5838	885.7490	0.0186
20-17P(1)	899.0152	901.2715	900.4973	900.5387	900.4880	0.0056
20-17P(2)	879.2274	881.4851	880.6678	880.7095	880.6680	0.0047
21-17R(0)	1003.7145	1006.8727	998.2631	998.3238	998.5330	0.0209
21-17R(1)	995.2344	998.4298	988.0571	988.1186	988.9930	0.0884
21-17R(2)	975.6874	978.9352	965.7496	965.8123	967.8110	0.2065
21-17P(1)	989.0216	992.1458	984.3439	984.4040	984.3300	0.0075
21-17P(3)	933.4837	936.6266	926.2577	926.3192	927.1920	0.0941
21-17P(4)	890.4729	893.6457	880.4657	880.5284	882.5230	0.2260
22-17R(0)	1018.0736	1021.6011	1006.8769	1006.9413	1006.9650	0.0024
22-17P(1)	1005.1215	1008.6131	994.1299	994.1940	994.1120	0.0082
22-17P(2)	980.6685	984.1649	969.4429	969.5072	969.5300	0.0024

the states $1s\sigma_g$ and $2p\sigma_u$ were included. For simplicity, terms proportional to the difference $(\varepsilon_k - \varepsilon_{k'})$ in Eq. (33) were neglected in calculations of the off-diagonal matrix elements of the expression $(-(1/2\mu)\tilde{\mathbf{B}} + \mathbf{I})$. This approximation is fully justified asymptotically, since the energies are degenerate. Table I demonstrates the good agreement between the two-state nonadiabatic results and experiment; the average discrepancy is of order 0.015%. In order to improve the accuracy of the calculations, more states should be included in the calculation, including Π states.¹⁶ In addition, a complete calculation of the \mathbf{I} matrix will increase the accuracy.

Relativistic corrections are found using a nonrelativistic zeroth-order Hamiltonian and first-order perturbation theory. The perturbation operator is given by

$$H^{\text{rel}} = \alpha^2 \left\{ -\frac{1}{2} \left[\varepsilon(R) + \frac{1}{r_A} + \frac{1}{r_B} \right]^2 + \frac{\pi}{2} [\delta(r_A) + \delta(r_B)] \right\}. \quad (41)$$

Here $\varepsilon(R)$ is the BO energy, α is the fine structure constant, $\alpha = e^2/(\hbar c)$, and δ is the Dirac delta function. For each vibronic level, the relativistic correction is obtained as a difference between the energies calculated with and without the relativistic Hamiltonian. These are considered rather accurate

and well established. Radiative corrections are based on calculations of the Bethe logarithm.^{16,19} Like the relativistic corrections, radiative corrections are obtained from calculations of the vibronic energies with and without the necessary corrections. In our calculations, radiative and relativistic corrections were taken as per reference¹⁶ and added to the two-state results.

VI. CONCLUSIONS

In this paper, the modified Born-Oppenheimer basis set (MBOB) method⁴ was developed and used to carry out calculations of the bound-state rovibronic energies of the hydrogen molecular ion and its isotopic variants. The issue of hermiticity was specifically addressed, and the equations were derived in an explicitly Hermitian form. The method was tested numerically and accurate results were obtained, showing an average error of calculated transition energies with respect to experimental results of 0.015%. The diagonalization of the nuclear Hamiltonian was performed using a Fourier grid Hamiltonian-discrete variable representation (FGH-DVR) method, which we generalized for this purpose to include a nonlinear grid and first derivative coupling term.

The derivation and calculations have led to the following conclusions:

- The modified Born-Oppenheimer basis set method is a useful method that provides deep insight into the coupling matrices involved in electronic transitions. It has been shown to be effective in predicting the correct behavior of the coupling matrices, and gave promising results for the transition energies of HD^+ within the ground state manifold.
- The matrix elements of the coupling matrices resulting from the MBOBS method are smaller in magnitude as compared with the corresponding matrix elements in the BOBS theory. This may lead to faster convergence with regard to the number of basis states included in the expansion as compared with the original BOBS method.
- The expansion in terms of $\sqrt{m/\mu}$ of the Hamiltonian, which was used in the derivation of Eq. (23), is such that hermiticity of the nuclear Hamiltonian matrix is not guaranteed.^{4,28} In Ref. 28, it was shown that this sort of error can not be ignored for the problems treated here. Consequently, the method was simplified by means of a state-independent scattering coordinate. Another solution to the problem could be the addition of higher terms to the expansion of the Hamiltonian. However, this adds to the complexity of the already complicated formulas. Thorson and co-workers have argued that probability is conserved even when the Hamiltonian is not Hermitian.^{37,38} However, it is not clear that the proof given by Delos and Thorson for this statement⁴⁶ is valid in the general case presented here.
- The use of a state-independent switching function simplifies the calculations significantly, and leads to accurate results. This conclusion is supported by the review of Errea and co-workers⁸ which shows that in a semi-

classical theory, the use of common translation factors as opposed to state-dependent translation factors leads to faster convergence.

Improvement of the method developed here can be carried out along the following lines:

- Calculation of the off-diagonal elements of the \mathbf{I} matrix will contribute to increased numerical accuracy of the calculations. Furthermore, the correct value of the off-diagonal matrix elements of the matrix \mathbf{I} will allow the correct estimation of the magnitude of the gerade-ungerade coupling terms for HD^+ .
- Calculations of angular coupling terms will open the way to calculate vibronic energies of excited states.
- Optimization of the computer codes to use less memory, so that larger basis set sizes could be used, is desirable.
- Generalizations of the formulas to include derivatives of the switching function will increase the accuracy of the calculations and possibly fix some of the symmetry problems when a state-dependent switching function is used.
- Finally, this method can be used to calculate vibronic energies of excited states (e.g., the $3d\sigma_g$ state). These are expected to be sensitive to the nonadiabatic coupling terms, and to the best of our knowledge, calculations beyond the adiabatic approximation were never performed for these states.

In the adiabatic BO representation, dynamics occurs because of nonadiabatic transitions induced by the nuclear kinetic energy operator; all other parts of the Hamiltonian (e.g., fine and hyperfine structure) are incorporated into the determination of the adiabatic potential energy surfaces. Hence, in order to do dynamics, it is essential to calculate the nonadiabatic matrix elements arising from the nuclear kinetic energy operator. Computer codes that calculate BO energies and wave functions using configuration-interaction self-consistent-field methods should *also* incorporate an option to calculate nonadiabatic coupling matrix elements since all dynamics involving curve crossing and asymptotic degeneracy are induced by these coupling matrix elements.

In the more general case of multielectron systems, efficient configuration interaction methods for calculating first and second nuclear derivative coupling matrix elements, incorporating the asymptotic motion of the electrons with the nuclei into the calculation of the nonadiabatic matrix elements, need to be developed. Asymptotic expansions of the molecular wave functions in terms of atomic basis functions in powers of $1/R$ may be sufficient to incorporate the asymptotic motion of the electrons with the nuclei.

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APPENDIX A: SEPARATION OF ANGULAR COORDINATES IN THE BOBS THEORY

Here we apply the separation of angular coordinates to the BOBS total wave function, and derive the radial Schrodinger equation. This separation is made possible by transforming the coordinate system from a space-fixed coordinate system to a molecule-rotating coordinate system.^{27,28} We further simplify the resulting coupling matrices by transformation of the electronic coordinates (x, y, z) to prolate spheroidal coordinates (ξ, η, χ) defined by

$$\begin{cases} x = \frac{1}{2}R \cos \chi \sqrt{(\xi^2 - 1)(1 - \eta^2)} \\ y = \frac{1}{2}R \sin \chi \sqrt{(\xi^2 - 1)(1 - \eta^2)} \\ z = \frac{1}{2}R \xi \eta. \end{cases} \quad (\text{A1})$$

The total wave function is expanded as follows:

$$\Psi(\vec{r}_g, \vec{R}) = \frac{1}{R} \sum_{\Lambda, k} \sum_{M_J} \varphi_{k\Lambda}^J(\xi, \eta, R) \Omega_{M_J, \Lambda}^J(\theta, \phi, \chi) G_{M_J}^J(R), \quad (\text{A2})$$

where the angular functions $\Omega_{M_J, \Lambda}^J(\theta, \phi, \chi)$ are given by

$$\Omega_{M_J, \Lambda}^J(\theta, \phi, \chi) = \frac{1}{2\pi} \exp(iM_J\phi) \exp(i\Lambda\chi) d_{M_J, \Lambda}^J(\theta).$$

The functions $d_{M_J, \Lambda}^J(\theta)$ satisfy the differential equation,

$$\left\{ \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + 2M_J\Lambda \frac{\cot \theta}{\sin \theta} - \frac{M_J^2 + \Lambda^2}{\sin^2 \theta} + J(J+1) \right\} d_{M_J, \Lambda}^J(\theta) = 0, \quad (\text{A3})$$

and the recursion relation,

$$\left\{ \pm \frac{\partial}{\partial \theta} - \Lambda \cot \theta + \frac{M_J}{\sin \theta} \right\} d_{M_J, \Lambda}^J(\theta) = \sqrt{(J \pm \Lambda + 1)(J \mp \Lambda)} d_{M_J, \Lambda \pm 1}^J(\theta). \quad (\text{A4})$$

Using the expansion in Eq. (A2), integration of Eq. (9) over

angular coordinates θ , ϕ and eventually also χ , is performed. The Hamiltonian is diagonal in both total angular momentum J and its projection along the nuclear axis M_J . From the above separation, one can show that matrix elements of the Hamiltonian which are off-diagonal with respect to the quantum number Λ (the eigenvalue of L_z) will vanish unless $\Lambda' = \Lambda, \Lambda \pm 1$. This originates from the integration over χ after integration over θ and ϕ is carried out. The electronic wave functions are identified by the united atom limit quantum numbers n , l and Λ (n and l are designated by the common index k , for simplicity of notation).^{4,30} The Schrodinger equation for the nuclear problem [Eq. (9)] can now be written in a more explicit way,

$$-\frac{1}{2\mu} \left[\mathbf{1} \left(\frac{d^2}{dR^2} - \frac{J(J+1) - 2\Lambda^2}{R^2} \right) + 2\mathbf{P}^{(R)} \frac{d}{dR} + \mathbf{B}^0 + \mathbf{D}^0 \right] \mathbf{G}_{M_J}^J = (\mathbf{1}E - \mathbf{U}) \mathbf{G}_{M_J}^J. \quad (\text{A5})$$

Here $\mathbf{P}^{(R)}$ is the radial part of the first derivative coupling term defined by

$$P_{k'\Lambda, k\Lambda}^{(R)} = \int d\vec{r}_g \varphi_{k'\Lambda} \left[\frac{\partial}{\partial R} \Big|_{x,y,z} - \frac{\lambda}{2} \frac{\partial}{\partial z} \right] \varphi_{k\Lambda}, \quad (\text{A6})$$

where the ξ and η part of the electronic wave function is denoted by $\varphi_{k,\Lambda} = \varphi_{k,\Lambda}(\xi, \eta, R)$. \mathbf{D}^0 is the off-diagonal in Λ coupling matrix originating from the angular terms of the nuclear kinetic energy operator $-\nabla_R^2/2\mu$ and the matrix $\vec{\mathbf{P}}$. \mathbf{B}^0 does not contribute to coupling terms off-diagonal in Λ , since the electronic basis functions depend only on the magnitude of the vector \vec{R} , and not on the angles θ and ϕ . We now complete the transformation to prolate spheroidal coordinates. Upon using commutation relations between the various operators,²⁸ the coupling terms in Eq. (A5) can be expressed by

$$\begin{aligned} P_{k'k}^{(R)} &= \int d\tau \varphi_{k'} \frac{\partial}{\partial R} \varphi_k + \frac{3}{2R} \delta_{k'k} + \frac{m}{2R} (\varepsilon_{k'} - \varepsilon_k) \\ &\times \int d\tau \varphi_{k'} r_g^2 \varphi_k + \frac{m\lambda R}{4} (\varepsilon_{k'} - \varepsilon_k) \\ &\times \int d\tau \varphi_{k'} \xi \eta \varphi_k, \end{aligned} \quad (\text{A7})$$

where the subscript Λ is omitted for simplicity and the diagonal element vanishes.⁴⁷ The matrix elements of \mathbf{B}^0 take the form

$$\begin{aligned} B_{k'k}^0 &= \int d\tau \varphi_{k'} \frac{\partial^2}{\partial R^2} \varphi_k + \frac{3}{R} \int d\tau \varphi_{k'} \frac{\partial}{\partial R} \varphi_k + \frac{m}{R} (\varepsilon_{k'} - \varepsilon_k) \int d\tau \varphi_{k'} r_g^2 \frac{\partial}{\partial R} \varphi_k - \frac{m}{R} \left(\frac{4}{R} \varepsilon_{k'} + \varepsilon_k' \right) \int d\tau \varphi_{k'} r_g^2 \varphi_k \\ &+ \frac{3m}{R^2} \int d\tau \varphi_{k'} r_g^2 V \varphi_k - \lambda \left[m \left(2\varepsilon_{k'} + \frac{R}{2} \varepsilon_k' \right) \int d\tau \varphi_{k'} \xi \eta \varphi_k - \frac{mR}{2} (\varepsilon_{k'} - \varepsilon_k) \int d\tau \varphi_{k'} \xi \eta \frac{\partial}{\partial R} \varphi_k \right. \\ &\left. - \frac{3m}{2} \int d\tau \varphi_{k'} \xi \eta V \varphi_k \right] - \frac{\lambda^2 m}{2} \left[\varepsilon_k \delta_{k'k} - \int d\tau \varphi_{k'} V \varphi_k \right], \end{aligned} \quad (\text{A8})$$

and on the diagonal, one obtains

$$B_{kk}^0 = - \int d\tau \left[\frac{\partial \varphi_k}{\partial R} \right]^2 + \frac{3}{2R^2} - \frac{m}{R} \left(\frac{4}{R} \varepsilon_k + \varepsilon'_k \right) \int d\tau \varphi_k r_g^2 \varphi_k + \frac{3m}{R^2} \int d\tau \varphi_k r_g^2 V \varphi_k + \frac{\lambda^2 m}{2} [\varepsilon_k + R \varepsilon'_k]. \quad (\text{A9})$$

Here the term proportional to λ in Eq. (A8) vanishes due to symmetry.⁴⁸ The formula for $B_{k'k}^0$ can be simplified when $\varepsilon_{k'} \neq \varepsilon_k$ such that the second derivative of the electronic wave function with respect to R need not be calculated.²⁸

Using Eqs. (A8) and (A7) we are now able to derive the following expression for the matrix $\tilde{\mathbf{B}}^0$ that appears in the radial Eq. (13),

$$\begin{aligned} \tilde{B}_{k'k}^0 (k' \neq k) = & - \int d\tau \frac{\partial \varphi_{k'}}{\partial R} \frac{\partial \varphi_k}{\partial R} + \frac{3m}{R^2} \int d\tau \varphi_{k'} r_g^2 V \varphi_k + \frac{m(\varepsilon_{k'} - \varepsilon_k)}{2R} \int d\tau r_g^2 \left(\varphi_{k'} \frac{\partial \varphi_k}{\partial R} - \frac{\partial \varphi_{k'}}{\partial R} \varphi_k \right) \\ & - \frac{m}{2R^2} [R(\varepsilon'_{k'} + \varepsilon'_k) + 4(\varepsilon_{k'} + \varepsilon_k)] \int d\tau \varphi_{k'} r_g^2 \varphi_k - m\lambda \left\{ \left[(\varepsilon_{k'} + \varepsilon_k) + \frac{R}{4}(\varepsilon'_{k'} + \varepsilon'_k) \right] \int d\tau \varphi_{k'} \xi \eta \varphi_k \right. \\ & \left. - \frac{3}{2} \int d\tau \varphi_{k'} \xi \eta V \varphi_k + \frac{R}{4}(\varepsilon_{k'} - \varepsilon_k) \left[\int d\tau \frac{\partial \varphi_{k'}}{\partial R} \xi \eta \varphi_k - \int d\tau \varphi_{k'} \xi \eta \frac{\partial \varphi_k}{\partial R} \right] \right\} + \frac{m\lambda^2}{2} \int d\tau \varphi_{k'} V \varphi_k. \quad (\text{A10}) \end{aligned}$$

On the diagonal, $\tilde{B}_{kk}^0 = B_{kk}^0$. Equation (A10) is general, and is valid also in the case of degeneracy. Moreover, using this formula, one need not calculate the second derivative with respect to R of the electronic wave function.

Finally, the off-diagonal in Λ coupling matrix \mathbf{D}^0 is given by

$$\begin{aligned} D_{k'\Lambda',k\Lambda}^0 = & \frac{1}{R^2} \left[\delta_{\Lambda',\Lambda-1} \sqrt{(J+\Lambda)(J-\Lambda+1)} - \frac{\delta_{\Lambda',\Lambda+1}}{R^2} \sqrt{(J-\Lambda)(J+\Lambda+1)} \right] \left[\mathcal{B}_{k'\Lambda',k\Lambda} + \frac{\lambda}{2} \mathcal{A}_{k'\Lambda',k\Lambda} \right] \\ & + \frac{1}{R^2} \left[\delta_{\Lambda',\Lambda-1} \sqrt{(J+\Lambda)(J-\Lambda+1)} + \frac{\delta_{\Lambda',\Lambda+1}}{R^2} \sqrt{(J-\Lambda)(J+\Lambda+1)} \right] \Lambda \\ & \times \int d\tau \varphi_{k'\Lambda'} \left(\xi \eta + \frac{\lambda}{2} \right) [(\xi^2 - 1)(1 - \eta^2)]^{-1/2} \varphi_{k\Lambda}, \quad (\text{A11}) \end{aligned}$$

where we have defined the following matrix elements:

$$\mathcal{B}_{k'\Lambda',k\Lambda} = \int d\tau \varphi_{k'\Lambda'} \frac{\sqrt{(\xi^2 - 1)(1 - \eta^2)}}{\xi^2 - \eta^2} \left(\eta \frac{\partial}{\partial \xi} \varphi_{k\Lambda} - \xi \frac{\partial}{\partial \eta} \varphi_{k\Lambda} \right), \quad (\text{A12})$$

$$\begin{aligned} \mathcal{A}_{k'\Lambda',k\Lambda} = & \int d\tau \varphi_{k'\Lambda'} \frac{\sqrt{(\xi^2 - 1)(1 - \eta^2)}}{\xi^2 - \eta^2} \left(\xi \frac{\partial}{\partial \xi} \varphi_{k\Lambda} - \eta \frac{\partial}{\partial \eta} \varphi_{k\Lambda} \right) \\ & = \frac{mR^2}{4} (\varepsilon_{k'} - \varepsilon_k) \int d\tau \varphi_{k'\Lambda'} \sqrt{(\xi^2 - 1)(1 - \eta^2)} \varphi_{k\Lambda} - \frac{1}{2} \int d\tau \varphi_{k'\Lambda'} [(\xi^2 - 1)(1 - \eta^2)]^{-1/2} \varphi_{k\Lambda}. \quad (\text{A13}) \end{aligned}$$

The last equation was simplified using commutation relations between the various operators.²⁸

APPENDIX B: DETAILED DERIVATION OF COUPLING MATRICES OF THE MBOBS METHOD

1. The first derivative matrix Π

Upon separation of angular coordinates, conversion into prolate spheroidal coordinates and using Eqs. (28) and (A7), the radial part of the first derivative matrix is obtained,

$$\begin{aligned} \Pi_{k'k}^{(R)} = & \int d\tau \varphi_{k'} \frac{\partial \varphi_k}{\partial R} + \frac{m(\varepsilon_{k'} - \varepsilon_k)}{2R} \int d\tau \varphi_{k'} r_g^2 \varphi_k \\ & - \frac{mR}{4} (\varepsilon_{k'} - \varepsilon_k) \int d\tau \varphi_{k'} f \xi \eta \varphi_k. \quad (\text{B1}) \end{aligned}$$

The diagonal matrix elements vanish, $\Pi_{kk}^{(R)} = 0$.

2. The second derivative matrix \mathbf{B}

From Eq. (29) we have

$$B_{k'k} = \int d\vec{r} \varphi_{k'}(\vec{r}, R) \left[\vec{\nabla}_R |_{\vec{r}_g} + \frac{f}{2} \vec{\nabla}_g \right]^2 \varphi_k(\vec{r}, R). \quad (\text{B2})$$

Basically, this is very similar to the BOBS \mathbf{B}^0 matrix, when λ is replaced by the negative of the switching function. The derivation of the matrix elements after integration over angular coordinates is thus very simple. The result obtained after some algebra is

$$B_{k'k} = \begin{cases} \int d\tau \varphi_{k'} \frac{\partial^2}{\partial R^2} \varphi_k + \frac{3}{R} \int d\tau \varphi_{k'} \frac{\partial}{\partial R} \varphi_k - \frac{m}{R} \left(\frac{4}{R} \varepsilon_{k'} + \varepsilon'_k \right) \int d\tau \varphi_{k'} r_g^2 \varphi_k \\ + \frac{m}{R} (\varepsilon_{k'} - \varepsilon_k) \int d\tau \varphi_{k'} r_g^2 \frac{\partial}{\partial R} \varphi_k + \frac{3m}{R^2} \int d\tau \varphi_{k'} r_g^2 V \varphi_k \\ + m \left[\left(2\varepsilon_{k'} + \frac{R}{2} \varepsilon'_k \right) \int d\tau \varphi_{k'} f \xi \eta \varphi_k \right. & k' \neq k \\ \left. - \frac{3}{2} \int d\tau \varphi_{k'} f \xi \eta V \varphi_k - \frac{R}{2} (\varepsilon_{k'} - \varepsilon_k) \int d\tau \varphi_{k'} f \xi \eta \frac{\partial \varphi_k}{\partial R} \right] \\ + \frac{m}{2} \left[\int d\tau \varphi_{k'} f^2 V \varphi_k - \varepsilon_k \int d\tau \varphi_{k'} f^2 \varphi_k \right] \\ \\ \frac{3}{2R^2} - \int d\tau \left(\frac{\partial \varphi_k}{\partial R} \right)^2 - \frac{m}{R} \left(\frac{4}{R} \varepsilon_k + \varepsilon'_k \right) \int d\tau \varphi_k r_g^2 \varphi_k \\ + \frac{3m}{R^2} \int d\tau \varphi_k r_g^2 V \varphi_k + m \left[\left(2\varepsilon_k + \frac{R}{2} \varepsilon'_k \right) \int d\tau \varphi_k f \xi \eta \varphi_k \right] & k' = k \\ - \frac{3m}{2} \int d\tau \varphi_k f \xi \eta V \varphi_k + \frac{m}{2} \left[\int d\tau \varphi_k f^2 V \varphi_k - \varepsilon_k \int d\tau \varphi_k f^2 \varphi_k \right] \end{cases} \quad (B3)$$

In the derivation of these formulas, we assumed that the result of operating with $\vec{\nabla}_g$ or $\vec{\nabla}_R$ on the switching function is negligible. Since the switching function becomes a constant asymptotically, this approximation is fully justified for large R . At small R , this approximation may create small errors, but as will be shown later, the asymptotic nature of the coupling matrix elements is the dominant factor in determining the bound-state energies. Moreover, this approximation significantly simplifies the derivation and the resulting formulas. Nevertheless, care must be taken when this approximation is used.

To within this approximation, one can conclude that the switching function commutes with the electronic Hamiltonian, $fh \approx hf$. Therefore matrix elements of the commutator $[f, h]$ between electronic basis states should vanish. This is a valid approximation as long as the two states being in-

tegrated over have the same symmetry. But, when different symmetry is involved and the states are not degenerate asymptotically (e.g., the states $1s\sigma_g$ and $3p\sigma_u$), the asymptotic result for the matrix element of the commutator is $\int d\tau \varphi_{1s\sigma_g} [f, h] \varphi_{3p\sigma_u} \rightarrow \varepsilon_{3p\sigma_u}(\infty) - \varepsilon_{1s\sigma_g}(\infty)$, which is a constant different than zero.

For an explicitly Hermitian form of the radial equation, the relevant matrix is $\tilde{\mathbf{B}} = \mathbf{B} - (d/dR)\mathbf{\Pi}^{(R)}$, not \mathbf{B} . Using Eqs. (B1), (B3) and the approximation

$$\begin{aligned} \int d\tau \varphi_{k'} f^2 h \varphi_k &\approx \frac{1}{2} \left[\int d\tau \varphi_{k'} f^2 h \varphi_k + \int d\tau \varphi_{k'} h f^2 \varphi_k \right] \\ &= \frac{1}{2} (\varepsilon_{k'} + \varepsilon_k) \int d\tau \varphi_{k'} f^2 \varphi_k, \end{aligned} \quad (B4)$$

we obtain a symmetric expression for $\tilde{\mathbf{B}}$,

$$\begin{aligned} \tilde{B}_{k'k} = B_{k'k} - \frac{d}{dR} \Pi_{k'k}^{(R)} &= - \int d\tau \frac{\partial \varphi_{k'}}{\partial R} \frac{\partial \varphi_k}{\partial R} + \frac{3m}{R^2} \int d\tau \varphi_{k'} r_g^2 V \varphi_k + \frac{m(\varepsilon_{k'} - \varepsilon_k)}{2R} \int d\tau \left(\varphi_{k'} \frac{\partial \varphi_k}{\partial R} - \frac{\partial \varphi_{k'}}{\partial R} \varphi_k \right) r_g^2 \\ &\quad - \frac{m}{2R^2} [R(\varepsilon'_{k'} + \varepsilon'_k) + 4(\varepsilon_{k'} + \varepsilon_k)] \int d\tau \varphi_{k'} r_g^2 \varphi_k \\ &\quad + \frac{m}{2} \left[\int d\tau \varphi_{k'} f^2 V \varphi_k - \frac{1}{2} (\varepsilon_{k'} + \varepsilon_k) \int d\tau \varphi_{k'} f^2 \varphi_k \right] + m \left(\varepsilon_{k'} + \varepsilon_k + \frac{R}{4} (\varepsilon'_{k'} + \varepsilon'_k) \right) \int d\tau \varphi_{k'} \xi \eta f \varphi_k \\ &\quad - \frac{3m}{2} \int d\tau \varphi_{k'} \xi \eta V f \varphi_k + \frac{mR}{4} (\varepsilon_{k'} - \varepsilon_k) \int d\tau \xi \eta f \left(\frac{\partial \varphi_{k'}}{\partial R} \varphi_k - \varphi_{k'} \frac{\partial \varphi_k}{\partial R} \right). \end{aligned} \quad (B5)$$

3. The electron reduced mass matrix I

The matrix \mathbf{I} is defined in Eq. (30), and derived in detail in Appendix C.

4. The angular coupling matrix \mathbf{D}

The matrix \mathbf{D} is constructed by operating with ∇_R^2 and $\vec{\nabla}_g \cdot \vec{\nabla}_R$ on the angular functions $\Omega_{M_J, \Lambda}^J$. Inserting the switching function as a coefficient of $\vec{\nabla}_g \cdot \vec{\nabla}_R$ (in analogy with λ in the BOBS theory), results in the angular contributions of the matrix $\vec{\mathbf{I}}$ and the nuclear kinetic energy operator. We thus obtain

$$D_{k'\Lambda', k\Lambda} = \frac{1}{2\pi} (\delta_{\Lambda', \Lambda+1} + \delta_{\Lambda', \Lambda-1}) \sum_{M_J} \int d\chi d\theta d\phi \int d\tau \varphi_{k'\Lambda'} \Omega_{M_J, \Lambda'}^J \left[\nabla_R^2 + \frac{f}{2} \vec{\nabla}_g \cdot \vec{\nabla}_R \right] \varphi_{k\Lambda} \Omega_{M_J, \Lambda}^J. \quad (\text{B6})$$

The factor of $1/2\pi$ compensates for the extra 2π factor contained in $d\tau$. After some algebra, we find

$$\begin{aligned} D_{k'\Lambda', k\Lambda} = & \frac{1}{R^2} \left[\delta_{\Lambda', \Lambda-1} \sqrt{(J+\Lambda)(J-\Lambda+1)} - \frac{\delta_{\Lambda', \Lambda+1}}{R^2} \sqrt{(J-\Lambda)(J+\Lambda+1)} \right] \left[\mathcal{B}_{k'\Lambda', k\Lambda}^f - \frac{1}{2} \mathcal{A}_{k'\Lambda', k\Lambda}^f \right] \\ & + \left[\delta_{\Lambda', \Lambda-1} \sqrt{(J+\Lambda)(J-\Lambda+1)} + \frac{\delta_{\Lambda', \Lambda+1}}{R^2} \sqrt{(J-\Lambda)(J+\Lambda+1)} \right] \frac{\Lambda}{R^2} \\ & \times \int d\tau \varphi_{k'\Lambda'} \left(\xi \eta - \frac{f}{2} \right) [(\xi^2 - 1)(1 - \eta^2)]^{-1/2} \varphi_{k\Lambda}, \end{aligned} \quad (\text{B7})$$

where [compare Eqs. (A12) and (A13)],

$$\mathcal{B}_{k'\Lambda', k\Lambda}^f = \int d\tau \varphi_{k'\Lambda'} \frac{\sqrt{(\xi^2 - 1)(1 - \eta^2)}}{\xi^2 - \eta^2} f \left(\eta \frac{\partial}{\partial \xi} \varphi_{k\Lambda} - \xi \frac{\partial}{\partial \eta} \varphi_{k\Lambda} \right), \quad (\text{B8})$$

and

$$\begin{aligned} \mathcal{A}_{k'\Lambda', k\Lambda}^f = & \int d\tau \varphi_{k'\Lambda'} \frac{\sqrt{(\xi^2 - 1)(1 - \eta^2)}}{\xi^2 - \eta^2} f \left(\xi \frac{\partial}{\partial \xi} \varphi_{k\Lambda} - \eta \frac{\partial}{\partial \eta} \varphi_{k\Lambda} \right) \\ = & \frac{mR^2}{4} (\varepsilon_{k'} - \varepsilon_k) \int d\tau \varphi_{k'\Lambda'} \sqrt{(\xi^2 - 1)(1 - \eta^2)} f \varphi_{k\Lambda} \end{aligned} \quad (\text{B9})$$

$$- \frac{1}{2} \int d\tau \varphi_{\Lambda'} [(\xi^2 - 1)(1 - \eta^2)]^{-1/2} f \varphi_{k\Lambda}. \quad (\text{B10})$$

The last equation was simplified using commutation relations.²⁸

APPENDIX C: DETAILED DERIVATION OF THE MATRIX \mathbf{I}

Here we derive an expression for the Hermitian matrix $[-(1/2\mu)\vec{\mathbf{B}} + \mathbf{I}]$. According to Eq. (30) the matrix element of the \mathbf{I} matrix is given by

$$\begin{aligned} I_{k'k} = & -\frac{m}{\mu} \left[-\frac{1}{2m} \langle k' | \left(\frac{f+\lambda}{2} \right)^2 \nabla_g^2 | k \rangle \right. \\ & \left. + \langle k' | \vec{s} \cdot \left(\vec{\nabla}_R | \vec{r} \left[V + \frac{1}{R} \right] \right) | k \rangle \right] \\ = & -\frac{m}{\mu} \left[\frac{m}{2} \langle k' | [h, \vec{s}]^2 | k \rangle + \langle k' | \vec{s} \cdot \left(\vec{\nabla}_R | \vec{r} \left[V + \frac{1}{R} \right] \right) | k \rangle \right] \\ = & \frac{1}{2\mu} \sum_j \vec{A}_{k'j} \vec{A}_{jk} - \frac{m}{2\mu} \langle k' | \vec{s} \cdot \left(\vec{\nabla}_R | \vec{r} \left[V + \frac{1}{R} \right] \right) | k \rangle \\ & - \frac{m}{2\mu} \langle k' | \left(\vec{\nabla}_R | \vec{r} \left[V + \frac{1}{R} \right] \right) \cdot \vec{s} | k \rangle, \end{aligned} \quad (\text{C1})$$

where derivatives of the switching function have been consistently neglected. In the last equation, we symmetrized the operator in order to make it Hermitian.⁷ We also used the

definition of the matrix $\vec{A}_{k'k} = -m \langle k' | [h, \vec{s}] | k \rangle$. Using Eq. (2), the identity $(\vec{\nabla}_R | \vec{r} V) = [\vec{\nabla}_R, h]$, the definitions for the matrix elements of $\vec{\mathbf{A}}$ and $\vec{\mathbf{P}}$ and inserting a complete set of states, we find

$$\begin{aligned} I_{k'k} = & \frac{1}{2\mu} \sum_j \vec{A}_{kj} \vec{A}_{jn} - \frac{m}{2\mu} \left(\varepsilon_{k'} + \varepsilon_k - \frac{2}{R^2} \right) s_{k'k}^R \\ & - \frac{m}{2\mu} (\varepsilon_k - \varepsilon_{k'}) \sum_j [\vec{s}_{k'j} \cdot \vec{P}_{jk} + \vec{P}_{k'j} \cdot \vec{s}_{jk}] \\ & + \frac{1}{2\mu} \sum_j [\vec{A}_{k'j} \cdot \vec{P}_{jk} + \vec{P}_{k'j} \cdot \vec{A}_{jk}]. \end{aligned} \quad (\text{C2})$$

Since $\vec{s}_{kj} = \vec{s}_{jk}$, $\vec{P}_{jk} = -\vec{P}_{jk}$ and $\vec{A}_{kj} = -\vec{A}_{jk}$, Eqs. (C2) represent the Hermitian matrix, but implementation of this formula requires the use of a complete set of states. Nevertheless, a complete set of states is not needed when a formula for $[-(1/2\mu)\vec{\mathbf{B}} + \mathbf{I}]$ is considered. Recalling the definition of \mathbf{B} [using Eqs. (28) and (B2)],

$$\begin{aligned}
B_{k'k} &= \langle k' | \left(\vec{\nabla}_R + \frac{f}{2} \vec{\nabla}_g \right)^2 | k \rangle \\
&= \sum_j \langle k' | \left(\vec{\nabla}_R + \frac{f}{2} \vec{\nabla}_g \right) | j \rangle \cdot \langle j | \left(\vec{\nabla}_R + \frac{f}{2} \vec{\nabla}_g \right) | k \rangle \\
&= \sum_j (\vec{P}_{k'j} + \vec{A}_{k'j}) \cdot (\vec{P}_{jk} + \vec{A}_{jk}) + \vec{\nabla}_R \cdot (\vec{P}_{k'k} + \vec{A}_{k'k}).
\end{aligned} \tag{C3}$$

We now define

$$\begin{aligned}
\tilde{B}_{k'k} &= B_{k'k} - \vec{\nabla}_R \cdot (\vec{P}_{k'k} + \vec{A}_{k'k}) \\
&= \sum_j (\vec{P}_{k'j} + \vec{A}_{k'j}) \cdot (\vec{P}_{jk} + \vec{A}_{jk}).
\end{aligned} \tag{C4}$$

Adding this result to Eq. (C2) results in

$$\begin{aligned}
& -\frac{1}{2\mu} \tilde{B}_{k'k} + I_{k'k} \\
&= -\frac{1}{2\mu} \sum_j \vec{P}_{kj} \vec{P}_{jn} - \frac{m}{2\mu} \left(\varepsilon_{k'} + \varepsilon_k - \frac{2}{R^2} \right) s_{k'k}^R \\
& \quad - \frac{m}{2\mu} (\varepsilon_k - \varepsilon_{k'}) \sum_j [\vec{s}_{k'j} \cdot \vec{P}_{jk} + \vec{P}_{k'j} \cdot \vec{s}_{jk}].
\end{aligned} \tag{C5}$$

This equation gives a Hermitian expression for $(-(1/2\mu)\tilde{\mathbf{B}} + \mathbf{I})$. A complete basis set of j states is still required in this expression, but this requirement can now be easily removed by noting that

$$\begin{aligned}
& \sum_j [\vec{s}_{k'j} \cdot \vec{P}_{jk} + \vec{P}_{k'j} \cdot \vec{s}_{jk}] \\
&= \langle k' | \vec{s} \cdot \left[\vec{\nabla}_R - \frac{\lambda}{2} \vec{\nabla}_g \right] | k \rangle + \langle k' | \left[\vec{\nabla}_R - \frac{\lambda}{2} \vec{\nabla}_g \right] \cdot \vec{s} | k \rangle.
\end{aligned} \tag{C6}$$

Finally, we obtain

$$\begin{aligned}
& -\frac{1}{2\mu} \tilde{B}_{k'k} + I_{k'k} \\
&= -\frac{1}{2\mu} \tilde{B}_{k'k}^0 - \frac{m}{2\mu} \left(\varepsilon_{k'} + \varepsilon_k - \frac{2}{R^2} \right) s_{k'k}^R - \frac{m}{2\mu} (\varepsilon_k - \varepsilon_{k'}) \\
& \quad \times \left\{ \langle k' | \vec{s} \cdot \left(\vec{\nabla}_R - \frac{\lambda}{2} \vec{\nabla}_g \right) | k \rangle + \langle k' | \left[\vec{\nabla}_R - \frac{\lambda}{2} \vec{\nabla}_g \right] \cdot \vec{s} | k \rangle \right\}.
\end{aligned} \tag{C7}$$

This expression is Hermitian and equivalent to Eq. (33).

¹M. Born and J. R. Oppenheimer, *Ann. Phys. (N.Y.)* **84**, 457 (1927).

²E. Merzbacher, *Quantum Mechanics* 2nd ed. (Wiley, New York, 1970), Chap. 5.

³B. H. Branden and M. R. C. McDowell, *Charge Exchange and the Theory of Ion-Atom Collisions* (Clarendon, Oxford, 1992).

⁴John B. Delos, *Rev. Mod. Phys.* **53**, 287 (1981).

⁵L. I. Ponomarev and S. I. Vinitzky, *J. Phys. B* **12**, 567 (1979); L. I. Ponomarev, S. I. Vinitzky, and F. R. Vukajlovic, *ibid.* **13**, 847 (1980); L.

I. Ponomarev, L. N. Somov, and F. Vukajlovic, *ibid.* **14**, 591 (1981).

⁶R. McCarroll and D. S. F. Crothers, *Adv. At., Mol., Opt. Phys.* **32**, 253 (1994).

⁷W. R. Thorson and J. B. Delos, *Phys. Rev. A* **18**, 117 (1978); **18**, 135 (1978).

⁸L. F. Errea, C. Harel, H. Jouin, L. Méndez, B. Pons, and A. Riera, *J. Phys. B* **27**, 3603 (1994).

⁹L. F. Errea, L. Mendez, and A. Riera, *J. Phys. B* **15**, 101 (1982).

¹⁰A. Riera, *Mol. Phys.* **88**, 199 (1996); J. F. Castillo, L. F. Errea, A. Macías, L. Méndez, and A. Riera, *J. Chem. Phys.* **103**, 2113 (1995).

¹¹Y. B. Band, *Phys. Rev. A* **8**, 243 (1973); **8**, 2857 (1973).

¹²D. M. Bishop and R. W. Wetmore, *Mol. Phys.* **26**, 145 (1973).

¹³D. M. Bishop, *Mol. Phys.* **28**, 1397 (1974).

¹⁴L. Wolniewicz and J. D. Poll, *Mol. Phys.* **59**, 953 (1986).

¹⁵L. Wolniewicz and T. Orlikowski, *Mol. Phys.* **74**, 103 (1991).

¹⁶R. E. Moss, *Mol. Phys.* **78**, 371 (1993).

¹⁷G. G. Balint-Kurti, R. E. Moss, I. A. Sadler, and M. Shaprio, *Phys. Rev. A* **41**, 4913 (1990).

¹⁸A. Carrington, I. R. McNab, and C. A. Montgomerie, *J. Phys. B* **22**, 3551 (1989).

¹⁹C. A. Leach and R. E. Moss, *Annu. Rev. Phys. Chem.* **46**, 55 (1995).

²⁰E. A. Soloviev and S. I. Vinitzky, *J. Phys. B* **18**, L557 (1985).

²¹J. Macek and K. A. Jerjian, *Phys. Rev. A* **33**, 233 (1986).

²²J. Macek, M. Cavagnero, K. Jerjian, and U. Fano, *Phys. Rev. A* **35**, 3940 (1987).

²³J. P. Davis and W. R. Thorson, *Can. J. Phys.* **56**, 996 (1978).

²⁴T. A. Green, *Phys. Rev. A* **23**, 519 (1981).

²⁵This is different from the notation of Carrington (Ref. 27), where \vec{R} was defined as the vector going from the lighter nucleus to the heavier one. Therefore, the operator $\vec{\nabla}_R$ has a different sign when the two notations are compared.

²⁶G. Hunter and H. O. Pritchard, *J. Chem. Phys.* **45**, 3806 (1966); **46**, 2146 (1967); **46**, 2153 (1967).

²⁷A. Carrington and R. A. Kennedy, *Gas Phase Ion Chemistry*, edited by M. T. Bower (Academic, New York, 1984), Vol. 3.

²⁸I. Tuvi, Ph.D. thesis, Ben-Gurion University, Beer-Sheva, Israel, 1998.

²⁹I. Tuvi and Y. B. Band, *J. Chem. Phys.* **107**, 9079 (1997).

³⁰J. D. Power, *Philos. Trans. R. Soc. London, Ser. A* **274**, 663 (1973).

³¹D. R. Bates, H. S. W. Massey, and A. L. Stewart, *Proc. R. Soc. London* **216**, 437 (1953); D. R. Bates, K. Lesham, and A. S. Stewart, *ibid.* **246**, 28 (1953).

³²G. Hadinger, M. Aubert-Frécon, and G. Hadinger, *J. Phys. B* **22**, 697 (1989).

³³G. Hadinger, A. Yanacopoulo, M. Aubert-Frécon, and G. Hadinger, *J. Phys. B* **23**, 1625 (1990).

³⁴A. Yanacopoulo, Ph.D. thesis, Lyon, France 1991.

³⁵A. Yanacopoulo, G. Hadinger, and M. Aubert-Frécon, *J. Phys. B* **22**, 2427 (1989).

³⁶J. Killingbeck, *Rep. Prog. Phys.* **48**, 54 (1985); *J. Phys. A* **18**, 245 (1985); *ibid.* **18**, L1025 (1985).

³⁷W. R. Thorson, M. Kimura, J. H. Choi, and S. K. Kundson, *Phys. Rev. A* **24**, 1768 (1981).

³⁸J. Rankin and W. R. Thorson, *Phys. Rev. A* **18**, 1990 (1978).

³⁹C. C. Marston and G. G. Balint-Kurti, *J. Chem. Phys.* **91**, 357 (1989).

⁴⁰D. T. Colbert and H. W. Miller, *J. Chem. Phys.* **96**, 1082 (1992).

⁴¹M. Monnerville and J. M. Robbe, *J. Chem. Phys.* **101**, 7580 (1994).

⁴²E. Fattal, R. Baer, and R. Kosloff, *Phys. Rev.* **53**, 1217 (1996).

⁴³M. P. Faifman, L. I. Ponomarev, and S. I. Vinitzky, *J. Phys. B* **9**, 2255 (1976).

⁴⁴L. I. Ponomarev, T. P. Puzynina, and L. N. Somov, *J. Phys. B* **10**, 1335 (1977).

⁴⁵L. I. Ponomarev, T. P. Puzynina, and N. F. Truskova, *J. Phys. B* **11**, 3861 (1978).

⁴⁶J. B. Delos and W. R. Thorson, *J. Chem. Phys.* **70**, 1774 (1979).

⁴⁷We have used the relation, $\int d\tau \varphi_i(\partial \varphi_i / \partial R) = -(3/2R)$.

⁴⁸The integral $\int d\tau \varphi_i \xi \eta \varphi_k = 0$ as a result of the integration over η . η is an antisymmetric function, and the integration boundaries are symmetric $[-1, 1]$. Therefore whether φ_k is symmetric or antisymmetric with respect to η , this integral vanishes identically.