Nonadiabatic coupling using a corrected Born-Oppenheimer basis: The vibronic spectrum of HD$^+$

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(Received 6 August 1998)

We apply a method suggested by Delos [Rev. Mod. Phys. **53**, 287 (1981)] to correct the Born-Oppenheimer basis by incorporation of proper boundary conditions for bound states of molecular systems. We calculate the correct nonadiabatic coupling matrix elements for H$_2^+$ and its isotopic variants and use them to determine the HD$^+$ vibronic spectrum. [S1050-2947(99)00504-1]

PACS number(s): 33.20.Vq, 31.10.+z, 31.30.−i, 31.70.−f

The Born-Oppenheimer (BO) approximation is fundamental to much of molecular quantum chemistry. Expanding the total wave function in terms of BO basis states allows one to include nonadiabatic effects representing the coupling between the nuclear motion and the electronic motion. However, when applied to molecular systems, e.g., H$_2^+$, the asymptotic motion of the electron with one of the nuclei is not incorporated correctly, resulting in incorrect boundary conditions on the wave function. In a semiclassical treatment, such problems can be overcome by introducing electron translation factors [1–5]. These factors, defined in terms of nuclear velocities, have no quantum equivalents. One way to include the effects of the motion of the electron with the nuclei in a quantum-mechanical framework is to introduce a generalized reaction coordinate which is a function of both the nuclear and electronic coordinates. This idea, discussed previously by Thorson and Delos [2], Davis and Thorson [6], Green [7], and Delos [1], has never been applied to bound-state calculations of molecular systems. In this paper we report our results of high-precision calculations of vibronic transition energies of the molecular hydrogen ion and its isotopic variants using a modified version of the theory of Delos [1]. It should be noted that although other methods exist to calculate high-precision vibronic transition energies of this system [8–10], their implementation to calculate bound states of excited electronic states is limited. The method presented here is general and can be used for all electronic states. The other methods are summarized in Refs. [11,12].

The Hamiltonian representing the two-nuclei, one-electron system, after separation of the center-of-mass motion, is given (in atomic units) by

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

Here $\vec{R}$ is the nuclear coordinate going from A to B. The electronic coordinate is chosen as $\vec{r}_g$, which connects the geometric center of the nuclei with the electron. $\vec{r}_A(\vec{r}_B)$ are vectors connecting nucleus $A(B)$ with the electron. $\vec{\nabla}_g$ and $\vec{\nabla}_R$ are the gradients with respect to the electronic and nuclear coordinates, respectively. μ is the reduced mass of the nuclei, m is the reduced electronic mass given by $m = m_e(M_A+M_B)/(m_e+M_A+M_B)$, and $\lambda = (M_A-M_B)/$

(M_A+M_B) is a positive mass asymmetry factor. In what follows we assume that $M_A \geq M_B$. The electronic Hamiltonian is given by $h = -(1/2m)\nabla_g^2 - [1/r_A + 1/r_B] = T + V$. We denote its set of eigenfunctions by the set $\{\varphi_k(\vec{r}_g,R)\}$. Nonadiabatic interactions are commonly introduced by expanding the total wave function $\Psi(\vec{r}_g,\vec{R})$ in terms of the Born-Oppenheimer basis-set (BOBS) functions:

$$\Psi(\vec{r}_g,\vec{R}) = \sum_k \varphi_k(\vec{r}_g,R)F_k(\vec{R}), \quad (2)$$

where $F_k(\vec{R})$ are the nuclear wave functions. This formulation is sometimes called perturbed stationary state (PSS) theory [14]. Using this expansion, the radial wave equation is given by

$$\left\{-\frac{1}{2\mu}[\mathbf{1}\vec{\nabla}_R^2 + 2\vec{\mathbf{P}}(R)\cdot\vec{\nabla}_R + \mathbf{B}^0(R)] + \mathbf{U}(R)\right\}\mathbf{F}(\vec{R}) = E\mathbf{F}(\vec{R}), \quad (3)$$

where $\vec{P}_{k'k} = \int d\vec{r}\,\varphi_{k'}(\vec{r},R)[\vec{\nabla}_R - (\lambda/2)\vec{\nabla}_g]\varphi_k(\vec{r},R)$ and $B^0_{k'k} = \int d\vec{r}\,\varphi_{k'}(\vec{r},R)[\vec{\nabla}_R - (\lambda/2)\vec{\nabla}_g]^2\varphi_k(\vec{r},R)$ are the first and second derivative coupling terms, and $\mathbf{U}$ is the potential. Standard scattering boundary conditions require that asymptotically, all coupling matrices will vanish. However, when applied to molecular systems such as H$_2^+$, these conditions are not fulfilled. This result stems from the fact that the individual terms of the expansion in Eq. (2) do not satisfy the scattering boundary conditions [1,13]. Asymptotically, the electron moves with one of the nuclei. This implies that an atomic basis which moves with the nuclei should be more suitable to describe the correct dynamics asymptotically. However, the BO basis-set functions are molecular in nature, therefore they fail to describe the correct physics asymptotically. The problem is evident when one tries to calculate $\vec{\mathbf{P}}$. As $R \rightarrow \infty$, $\vec{P}_{k'k}(R) \rightarrow$ const, which is not necessarily zero. Furthermore, matrix elements of $\vec{\mathbf{P}}$ between states with different parity (g,u) do not vanish as they should, and give rise to non-negligible fictitious contributions. This is particulary important in the ground-state manifold of HD$^+$, where the only contribution to the matrix $\vec{\mathbf{P}}$ is fictitious.

Steps to overcome these problems have been taken by Thorson and Delos [2] and Davis and Thorson [6]. Delos [1]

generalized those methods and developed a theory in which the effect of the asymptotic motion of the electrons with the nuclei is treated quantum mechanically. A generalized scattering coordinate which is a function of both the nuclear coordinate and the electronic coordinate is used. In this theory, which we call the modified Born-Oppenheimer basis-set (MBOBS) method, the problems of the BOBS theory discussed above are eliminated. The generalized scattering coordinate is constructed using a switching function that describes an electron translation and 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. To the best of our knowledge, applications of these methods were not performed in the context of bound-state energies of the hydrogen molecular ion nor any other molecular system. An outline of the theory is drawn below. Details can be found in Refs. [15,16] .

Three different Jacobi sets of coordinates can be used to describe the one-electron two-nuclei system at different stages of the scattering process, in which the electron is bound to nucleus A, B, or both. A realistic scattering 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 ($\vec{R}_i$ being the coordinate of the electron to nucleus i). One can therefore 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 [1] we thus define the scattering coordinate to be $\vec{\tilde{R}}(\vec{r}, \vec{R})$. In general, the coordinate $\vec{\tilde{R}}$ could be state-dependent. However, in such cases, Hermiticity of the resulting Hamiltonian cannot be assured. A complete treatment with a state-dependent scattering coordinate can be found in Ref. [15]. In the calculations we present here, we have taken $\vec{\tilde{R}}$ as state-independent. The BOBS expansion of the total wave function is thus replaced by the ansatz

$$\Psi(\vec{r}_g, \vec{R}) = \sum_k \hat{\varphi}_k(\vec{r}_g, \tilde{R}) F_k(\vec{\tilde{R}}). \qquad (4)$$

If the basis-set functions $\{\hat{\varphi}_k(\vec{r}_g, \tilde{R})\}$ are of atomic character (i.e., single-center functions), 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), $\vec{\tilde{R}}$ must be a curvilinear coordinate. In general, $\vec{\tilde{R}}$ can be written as

$$\vec{\tilde{R}}(\vec{r}_g, \vec{R}) = \vec{R} + \frac{m}{\mu}\vec{s}(\vec{r}_g, \vec{R}), \qquad (5)$$

where $\vec{s}$ is chosen to be of the form $\vec{s} = \frac{1}{2}[f(\vec{r}_g, R) + \lambda]\vec{r}_g - \frac{1}{8}(1 - \lambda^2)\vec{R}$. Here $f(\vec{r}_g, R)$ is a switching function which is antisymmetric with respect to the electronic coordinate $\vec{r}_g$, and as $R \rightarrow \infty, f \rightarrow \pm 1$. With this choice of heavy particle coordinate, $\vec{\tilde{R}}$ is proportional asymptotically to $\vec{R}_i (i = A, B)$. This particular choice of scattering coordinate in a classical

theory has resolved many of the problems of the BOBS theory [1]. However, there is still freedom in the choice of the switching function.

A complete derivation of the coupled equations resulting from Eq. (4) is presented in Ref. [16]. Here we summarize the main steps. First, the original BO basis set $\{\varphi_k(\vec{r}_g, R)\}$ is mapped to create the new basis set $\{\hat{\varphi}_k(\vec{r}_g, \tilde{R})\}$. In the second step, the total Hamiltonian is written in terms of the new coordinate $\vec{\tilde{R}}$. The resulting expression is then expanded in powers of $\sqrt{m/\mu}$, which, from a semiclassical point of view, is proportional to the nuclear velocity divided by the electronic velocity. For simplicity, terms of the order $(m/\mu)^{3/2}$ ($\approx 10^{-5}$ for H_2^+) and higher powers are consistently neglected. In addition, terms of order m/μ which are also proportional to derivatives of the switching function or related factors [e.g., $(f^2 - 1)$] are also neglected. Finally, one should note that for the purpose of numerical integration over electronic coordinates, $\tilde{R}$ is a dummy integration variable. It is therefore designated for convenience by R in what follows. A new set of coupled equations for the radial wave function results, very similar to the original BOBS radial Eq. (3),

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

$$= E\mathbf{F}(\vec{R}), \qquad (6)$$

where $\mathbf{U}$ is as before; and to within approximations already made, the new coupling matrices are given by

$$\Pi_{k'k} = \int d\vec{r}\, \varphi_{k'}(\vec{r}_g, R)\left(\vec{\nabla}_R - \frac{\lambda}{2}\vec{\nabla}_g - m[h, \vec{s}] \right)\varphi_k(\vec{r}_g, R),$$

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

$$I_{k'k} = \frac{1}{2\mu}\int d\vec{r}\, \varphi_{k'}(\vec{r}_g, R)\left\{ (f + \lambda)\nabla_g^2 \right.$$

$$\left. - 2m\,\vec{s} \cdot \left[\vec{\nabla}_R\left(V + \frac{1}{R} \right) \right] \right\} \varphi_k(\vec{r}_g, R). \qquad (7)$$

The first and second derivative coupling matrices ($\vec{\mathbf{\Pi}}$ and $\mathbf{B}$) that appear in Eq. (6) are similar to the BOBS coupling matrices ($\vec{\mathbf{P}}$ and $\mathbf{B}^0$), except the new matrices obey the scattering boundary conditions and vanish asymptotically. The matrix $\mathbf{I}$ is the electron reduced mass coupling matrix originating from differences between asymptotic electronic reduced masses. In the molecular BO basis-set framework 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 $\mathbf{I}$ is proportional to the difference between these reduced masses, and is therefore very small. A detailed derivation of these coupling matrices can be found in Refs. [15,16].

The solution of Eq. (6) is performed in several steps. (a) The eigenfunctions and eigenenergies of the electronic Hamiltonian h are found. This is carried out by transforming the problem into prolate spheroidal coordinates, $\vec{r}_g$
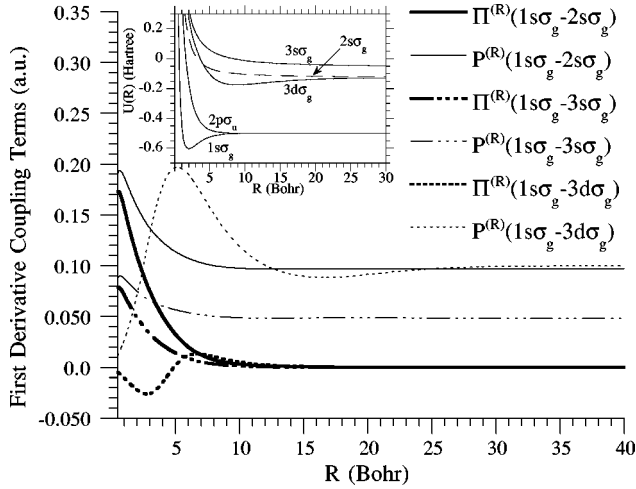
FIG. 1. Comparison between matrix elements of the BOBS and MBOBS radial first derivative matrices for HD^+, for various σ_g states. Inset shows the relevant potential-energy surfaces.

$=(\xi,\eta,\chi)$, in which the electronic Hamiltonian is separable. In our calculations, we used the algorithm of Hadinger and co-workers, which is based on the Killingbeck method associated with Miller's algorithm [17–19]. (b) Equation (6) is converted to a radial equation by transformation to a rotating coordinate system, expansion of the wave function in symmetric top functions, and integration over angular coordinates (see, for example, [15,20]). The radial equation is then solved to obtain the bound-state energies and the wave function. This is performed using a specially designed Fourier grid Hamiltonian–discrete variable representation (FGH-DVR) scheme [21].

The switching function was determined using the method of Thorson and co-workers [22]. It was chosen to have the analytic form $f(\eta,R)=\tanh[b(R)R\eta]$, where the function $b(R)$ was determined so that the magnitude of the corrected coupling matrices of the ground state to higher-lying states as compared with the BOBS coupling matrices was minimized. The function $b(R)$ was determined empirically on a grid of points in R, and was then interpolated to obtain its value for any given R. For simplicity, derivatives of the switching function have been consistently neglected.

The issue of Hermiticity requires special attention in formulating this theory, since the DVR method can lead to significant numerical errors if the Hamiltonian matrix is not written in an explicitly Hermitian form [21]. Therefore, when deriving specific formulas, each coupling matrix should be examined carefully. Since all operators and basis-set functions are real, one should require that the nuclear Hamiltonian be symmetric with respect to interchanging basis-set indices. Such Hermitian formulas have been derived for each coupling matrix [15,16].

The MBOBS method was used to calculate vibration-rotation energies of the hydrogen molecular ion and its isotopic variants (H_2^+,HD^+,D_2^+). Figure 1 presents a comparison between several matrix elements of the radial parts of the matrices $\vec{\Pi}$ and $\vec{P}$. The inset shows the relevant potential- energy curves. The most important difference between the BOBS results and the MBOBS results, as is evident from Fig. 1, is the asymptotic limit of the matrix elements. In addition, the matrix elements of $\Pi^{(R)}$ are smaller in magnitude as compared with the matrix elements of $P^{(R)}$. These results suggest that convergence with respect to basis-set size can be much faster in the MBOBS method.

We calculated vibronic transition energies for HD^+ and compared them with experimental results. 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 several transition energies (the lowest and highest experimentally determined ones) including Born-Oppenheimer, adiabatic, and two-state nonadiabatic calculation of the transition frequencies of HD^+ and their comparison to experimental values. Radiative and relativistic corrections (including hyperfine effects [23]) were taken as per Ref. [10] and added to the two-state results. The two-state nonadiabatic calculation was performed within the $1s\sigma_g$ and $2p\sigma_u$ manifold of HD^+. The matrix $\mathbf{I}$ was estimated by its asymptotic value. Table I demonstrates the agreement between the two-state nonadiabatic results and experiment; the average discrepancy of all of our results is of order 0.015%. In order to improve the accuracy of the cal-

TABLE I. BO, adiabatic, nonadiabatic two-state, radiatively and relativisitically corrected nonadiabatic two-state, and experimental transition frequencies of HD^+ in cm^{-1}. Percent difference refers to the difference between the radiatively and relativisitically corrected two-state nonadiabatic calculations and experimental values. Experimental values are taken from Ref. [10].

Transition	BO	Adiabatic	Two-state	Corrected two-state	Experiment	% difference
1-0 P(1)	1869.7222	1869.1685	1869.1683	1869.2044	1869.1340	0.0038
1-0 P(2)	1824.1013	1823.5666	1823.5664	1823.5453	1823.5330	0.0007
1-0 P(3)	1777.0063	1776.4916	1776.4914	1776.4717	1776.4590	0.0007
2-1 R(0)	1857.3311	1856.8028	1856.8025	1856.7798	1856.7780	0.0001
3-2 R(0)	1762.0999	1761.6312	1761.6309	1761.6106	1761.6160	0.0003
3-2 R(1)	1798.0181	1797.5370	1797.5366	1797.5153	1797.5220	0.0004
3-2 R(2)	1831.5890	1831.0970	1831.0967	1831.0744	1831.0830	0.0005
3-2 P(2)	1642.5451	1642.1220	1642.1217	1642.1047	1642.1080	0.0002
22-17 R(0)	1018.0736	1021.6011	1006.8769	1006.9413	1006.9650	0.0024
22-17 P(1)	1005.1215	1008.6131	994.1299	994.1940	994.1120	0.0082
22-17 P(2)	980.6685	984.1649	969.4429	969.5072	969.5300	0.0024

culations, more states should be included in the calculation, including Π states [10]. In addition, a complete calculation of the **I** matrix will increase the accuracy.

To conclude, the modified Born-Oppenheimer basis-set (MBOBS) method was adapted for calculating bound-state energies of the molecular hydrogen ion and its isotopic variants. The nuclear derivative coupling matrices were calculated in a manner so as to give their correct asymptotic behavior. Our results show that the coupling matrices are smaller in magnitude than the BOBS coupling matrices, and therefore faster convergence of bound-state energies as a function of basis-set size is expected. This method can be used to include nonadiabatic effects when bound-state energies of higher-lying electronic states are calculated.

For multielectron systems, efficient configuration-interaction methods for calculating first and second nuclear derivative coupling matrix elements need to be developed, where these matrix elements include the modifications necessary to incorporate the asymptotic motion of the electrons with the nuclei into the calculation of the nonadiabatic matrix elements. Initial steps along these lines have been taken [5,24].

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