Adiabatic Jacobi corrections for H$_2^+$-like systems

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The Coulomb three-body problem in Jacobi coordinates was solved by treating the distance of the particles having equal charge as a parameter. This method allows computation of electronic energies with finite nuclear masses while maintaining the notion of a potential energy curve. The rotationless ground-state electronic and the so-called adiabatic Jacobi correction (AJC) energies are presented for H$_2^+$, D$_2^+$, and HD$^+$ at fixed internuclear separations. The AJCs are defined as the difference between the results obtained from calculations using proper finite and infinite nuclear masses. Except at the united atom limit, the AJCs are smaller than the traditional first-order diagonal Born-Oppenheimer corrections. Expectation values of proton-electron, *p-e*, and deuteron-electron, *d-e*, distances for HD$^+$ have been computed as a function of internuclear separation. Similarly to the fully nonadiabatic approach, the present method is able to follow the symmetry breaking in HD$^+$. Exact and approximate analytical and numerical results are given for counterfactual systems as well. In these cases changes are allowed for the values of the electron rest mass or the elementary charge, as well as for the mass or charge of the unique particle (electron). © *2007 American Institute of Physics.* [DOI: 10.1063/1.2406068]

I. INTRODUCTION

The three-body problem with Coulomb interactions has been much studied in atomic and molecular physics as the most tractable problem in which the more general features of atomic and molecular structures are exhibited.[1–5]

To put this problem in its general context and to establish our notation, let the laboratory-fixed coordinates for the three particles be denoted as $\mathbf{x}_i$, $i=1,2,3$, where $\mathbf{x}_i$ is a (3×1) column matrix of Cartesian components $x_{\alpha i}$, $\alpha = x$, y, or z. To avoid the completely continuous part of the spectrum of the three-body Schrödinger Coulomb Hamiltonian, the translational motion is separated from the full Hamiltonian by using the center-of-mass coordinate $\mathbf{X}$ and two translation-free coordinates $\mathbf{t}_i$, $i=1,2$.[6]

The translationally invariant part of the kinetic energy operator is

$$\hat{K}(\mathbf{t}) = \frac{-\hbar^2}{2} \sum_{i,j=1}^{2} \frac{1}{\mu_{ij}} \nabla(\mathbf{t}_i) \cdot \nabla(\mathbf{t}_j), \qquad (1)$$

where $\nabla(\mathbf{t}_i)$ is the usual grad operator expressed in the variable $\mathbf{t}_i$.

Let us limit our attention to systems with three unit charges with the particle of mass m_1 having the negative (positive) unit charge and the other two, with masses m_2 and m_3, chosen to have positive (negative) charges. Choose $\mathbf{t}_1$ as the interparticle vector for the two particles of equal charge

and $\mathbf{t}_2$ as the vector to the remaining particle from the center of mass of the two particles of equal charge (these are Jacobi coordinates, a special case of general orthogonal coordinates[6]). Then,

$$\frac{1}{\mu_1} = \frac{m_2 + m_3}{m_2 m_3}, \quad \frac{1}{\mu_2} = \frac{1}{m_1} + \frac{1}{m_2 + m_3}, \quad \frac{1}{\mu_{12}} = 0, \qquad (2)$$

and the Hamiltonian operator becomes

$$\hat{H}_{\text{mol}} = \frac{-\hbar^2}{2} \sum_{i=1}^{2} \frac{1}{\mu_i} \nabla^2(\mathbf{t}_i)$$
$$+ \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{|\mathbf{t}_1|} - \frac{1}{|m_+\mathbf{t}_1 + \mathbf{t}_2|} - \frac{1}{|m_-\mathbf{t}_1 - \mathbf{t}_2|} \right), \qquad (3)$$

where $m_+ = m_3/(m_2+m_3)$ and $m_- = m_2/(m_2+m_3)$. If m_3 is chosen to be dm_2, then

$$m_+ = \frac{d}{1+d}, \quad m_- = \frac{1}{1+d}, \qquad (4)$$

so that the potential term in (3) depends only on the relative masses of the two particles of equal charge. $\hat{H}_{\text{mol}}$ is also completely expressible in terms of the internal coordinates,

$$R_1 = |\mathbf{t}_1|, \quad R_2 = |\mathbf{t}_2|, \quad \text{and} \quad \Theta, \quad \text{where} \quad \mathbf{t}_1^T \mathbf{t}_2 = R_1 R_2 \cos \Theta. \qquad (5)$$

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The operator $\hat{H}_{\text{mol}}$ can be shown to be both Hermitian and self-adjoint. The proof of this, first shown in 1951 by Kato[7] (see also Thirring[8]), depends on the fact that the potential operator is, in a well-defined sense, small compared to the kinetic energy operator. It is only for a self-adjoint operator that it can be shown that normalization of the wave function will be preserved. Self-adjointness is the same as hermiticity for a finite-dimensional operator but is a stronger condition for continuous operators such as the Hamiltonian. The spectrum of the Coulomb Hamiltonian can have two parts: a discrete part, consisting of all isolated eigenvalues of countable multiplicity, and an essential part, which is the complement of the discrete part. The discrete part describes the bound states of the system, and the essential part describes both the metastable and scattering states of the system. The essential spectrum begins at the energy of the lowest two-body cluster decomposition of the system. This is a consequence of the Hunziker–Van Winter–Zhislin (HVZ) result which is proved as Theorem XIII.17 in Ref. 9. Whether or not a given three-particle Hamiltonian has any discrete spectrum is a matter that requires careful study of the individual problem and few general results are known. At present what is known for these and other few-body problems is surveyed in the review by Armour *et al.*[1] What happens to the discrete spectrum in the cases where first one and then two nuclear masses are increased without limit is discussed by Frolov[10] in a study of the hydrogen molecular ion. He showed that when one mass is increased without limit, any discrete spectrum persisted, but when two masses were allowed to increase without limit, the Hamiltonian ceased to be well-defined and this failure led to what he called *adiabatic divergence* in attempts to compute discrete eigenstates.

A paper that appears to have rather similar aims to the present one, by Takahashi and Takatsuka,[11] uses a semiclassical theory to describe the motion of the unique charged particle. It also deploys ordinary perturbation theory as used by Born and Oppenheimer to account for the fact that in their calculations the error in the Born-Oppenheimer approximation seems to scale as $m_1^{3/2}$, and that the fifth-order term in the expansion vanishes. While not doubting the results of their calculations, the perturbation theoretical analysis offered by them for their form must be regarded as of doubtful validity since it can be shown[12] that the Born-Oppenheimer perturbation is singular and cannot be considered by using an ordinary perturbation theory.

Here, however, the full three-body problem will not be considered and the approach of Wolniewicz and Poll[13] will be pursued but not, however, to the same accuracy. Although the present formulation is, in principle, capable of yielding wave functions and energies for the full three-body system, much as in Refs. 14–16, the choice of Jacobi coordinates is not one that is usually made if that is the goal. The advantage of Jacobi coordinates for our purposes is that the internuclear distance is a variable in the formulation. It would also be a variable if interparticle coordinates had been chosen, but in this system the integration ranges are entangled and if choices are made to disentangle the ranges by, for example, the choice of perimetric coordinates, the separation of the various kinds of internal motion is obscured. The aim of this study will be to perform consistent converged calculations at various values of the internuclear parameter for different choices of the particle masses to show what happens both to the energies and the wave functions for the particular choices.

Our calculations are performed in a frame located in the molecule but with fixed values of R_1. It is thus not necessary to treat the nuclear masses as infinite as is the custom in traditional electronic structure calculations. However, as we shall not consider rotational motions ($J=0$), if we were to allow the nuclear masses to increase without limit, then our results would exactly match the traditional clamped nuclei calculation results to within computational accuracy. Traditionally, a first-order perturbative energy correction, the so-called diagonal Born-Oppenheimer correction (DBOC), has been advocated[17–22] to move simply beyond the BO approximation in standard clamped nuclei calculations. The DBOC is defined by means of

$$E_{\text{DBOC}}(\mathbf{X}) = -\frac{1}{2}\sum_{a=1}^{A}\langle\psi(\mathbf{x},\mathbf{X})|\frac{\nabla^2(\mathbf{X}_a)}{M_a}|\psi(\mathbf{x},\mathbf{X})\rangle_{\mathbf{x}},\qquad(6)$$

where $\psi(\mathbf{x},\mathbf{X})$ is the electronic wave function calculated in the clamped nucleus approximation. The electronic coordinates are designated as $\mathbf{x}$, and the A sets of nuclear coordinates (in the present case $A=2$) are designated as $\mathbf{X}$. This is the leading term in the corrections arising in the Born-Huang approach[23] to the separation of electronic and nuclear motion. It is regarded as modifying the potential energy as calculated in the clamped nuclei approximation. In the case of an atom there is only one nucleus and that is placed at the origin of coordinates in a clamped nuclei calculation so that the DBOC can be realized as a number. It is easy to show in the case of the hydrogen atom that the so calculated DBOC corrects the clamped nucleus energy to the energy that would be calculated if the reduced mass was used in the full calculation. That is, it describes the internal motion correctly after the separation of translations. In the present formulation it is perfectly possible to calculate the results both for the infinite and the correct nuclear masses and hence to construct an adiabatic Jacobi correction (AJC), which should be the same as the DBOC if it really accounts for translational motion in the case of a molecule.

The wave functions resulting from the present approach can be used to compute different expectation values which can be compared to expectation values from the full nonadiabatic solution of the same problem made recently by Bubin *et al.*[24]

II. SOLUTION OF THE COULOMB TWO-BODY PROBLEM IN JACOBI COORDINATES

The Jacobi coordinate system offers the advantage that it is straightforward to fix the distance of the two nuclei by fixing the R_1 coordinate. In the case of $J=0$, where J is the usual rotational quantum number, the resulting two-dimensional Hamiltonian is given as

$$\hat{H} = \hat{K} + V_{23} - V^+(R_2, \Theta) - V^-(R_2, \Theta), \tag{7}$$

with

$$\hat{K} = -\frac{1}{2\mu_2}\frac{\partial^2}{\partial R_2^2} - \left(\frac{1}{2\mu_1 R_1^2} + \frac{1}{2\mu_2 R_2^2}\right)\left(\frac{\partial^2}{\partial \Theta^2} + \cot\Theta\frac{\partial}{\partial\Theta}\right), \tag{8}$$

$$V_{23} = \frac{1}{R_1}, \quad \text{and}$$

$$V^\pm(R_2, \Theta) = \frac{1}{\sqrt{(m_\pm R_1)^2 + R_2^2 \pm 2m_\pm R_1 R_2 \cos\Theta}}. \tag{9}$$

The integration volume over the internal coordinates is $\sin\Theta d\Theta dR_2$, because the radial part of the Jacobian has been included in the internal motion trial function. In this section a practical method is presented for solving the Schrödinger equation corresponding to $\hat{H}$ using a variational technique.

A. Basis functions

Let us define a two-dimensional basis $\{\chi_{n_2}(R_2)P_l(\cos\Theta)\}$, where n_2 runs from 0 to N_2-1 and l runs from 0 to $L-1$. This is a direct product basis of one-dimensional radial functions and one-dimensional angular functions. The choice of the normalized orthogonal Legendre polynomials $P_l(\cos\Theta)$ is explained as follows. First, one has to handle the singularity present in the Θ-dependent part of the kinetic energy operator. The Legendre polynomials can treat this singularity, which occurs at linear geometries, because they are analytic eigenfunctions of the Θ-dependent part of the kinetic energy operator. Second, one has to find a suitable basis for setting up the matrix representation of the potential energy operator. As it will be introduced in Sec. II C, the Legendre polynomials satisfy this requirement as well.

Due to the radial singularity present in the $1/R_2^2$ term of the kinetic energy operator, the radial basis functions $\chi_{n_2}(R_2)$ have to be suitable for treating this singularity. Let us consider different choices for the radial basis functions.

1. An orthogonal basis set

Let us define $\chi_{n_2}(R_2) = N_{n_2}^{-1/2}K^{3/2}R_2 L_{n_2}^{(2)}(KR_2)$ $\times\exp(-KR_2/2)$ with $N_{n_2}=(n_2+2)(n_2+1)$, where the $L_n^{(2)}(x)$ functions are the associated Laguerre polynomials, and K is a positive real parameter. The $L_n^{(2)}(x)$ are orthogonal in the interval $[0,\infty]$ with the weight function $x^2 \exp(-x)$. Therefore, the above defined radial basis functions are orthogonal and they are able to treat the radial singularity in the kinetic energy operator, because the matrix elements, which can be defined by a nonsingular integral using these basis functions, of the singular term can be computed by employing the following analytical formula [only the upper triangle elements $(n_2'\geqslant n_2)$ of the symmetric matrix]:

$$(\mathbf{R}_2^{-2})_{n_2,n_2'} = \langle\chi_{n_2}(R_2)|\frac{1}{R_2^2}|\chi_{n_2'}(R_2)\rangle$$

$$= \int_0^\infty N_{n_2}^{-1/2}N_{n_2'}^{-1/2}K^3 L_{n_2}^{(2)}(KR_2)L_{n_2'}^{(2)}(KR_2)$$

$$\times\exp(-KR_2)dR_2$$

$$= N_{n_2}^{1/2}N_{n_2'}^{-1/2}\frac{K^2}{6}(3n_2' - n_2 + 3). \tag{10}$$

Computation of the matrix elements of the radial differential operator of the Hamiltonian can also be done analytically, and the upper triangle elements $(n_2'\geqslant n_2)$ of the symmetric matrix can be given as

$$(\mathbf{K}_{R_2})_{n_2,n_2'} = \langle\chi_{n_2}(R_2)|\frac{\partial^2}{\partial R_2^2}|\chi_{n_2'}(R_2)\rangle$$

$$= -N_{n_2}^{1/2}N_{n_2'}^{-1/2}\frac{K^2}{12}(4n_2 + 6 - 3\delta_{n_2,n_2'}). \tag{11}$$

2. A nonorthogonal basis set

Let us define $\chi_{n_2}(R_2)=K^{1/2}R_2 L_{n_2}(KR_2)\exp(-KR_2/2)$, where the $L_n(x)$ functions are the Laguerre polynomials and K is a positive real parameter. The $L_n(x)$ are orthogonal in the interval $[0,\infty]$ with the weight function $\exp(-x)$. These radial basis functions are nonorthogonal and their overlap integrals can be given by a simple analytical formula (only the upper triangle elements $(n_2'\geqslant n_2)$ of the symmetric matrix),

$$(\mathbf{S})_{n_2,n_2'} = \langle\chi_{n_2}(R_2)|\chi_{n_2'}(R_2)\rangle$$

$$= \frac{1}{K^2}(6n_2^2 + 6n_2^2 + 2)\delta_{n_2,n_2'}$$

$$- \frac{4}{K^2}(n_2 + 1)^2\delta_{n_2+1,n_2'}$$

$$+ \frac{1}{K^2}(n_2 + 1)(n_2 + 2)\delta_{n_2+2,n_2'}. \tag{12}$$

Due to the multiplication of the orthogonal Laguerre functions with R_2 the radial basis functions become nonorthogonal, however, they have the advantage that they are able to treat the radial singularity in the kinetic energy operator by cancelling the $1/R_2^2$ term. The matrix elements of the singular operator are defined simply by the overlap integrals of the orthogonal Laguerre polynomials resulting in a unit matrix,

$$(\mathbf{R}_2^{-2})_{n_2,n_2'} = \langle\chi_{n_2}(R_2)|\frac{1}{R_2^2}|\chi_{n_2'}(R_2)\rangle = \delta_{n_2,n_2'}. \tag{13}$$

Computation of the matrix elements of the radial differential operator of the Hamiltonian can also be done analytically, and the upper triangle elements $(n_2'\geqslant n_2)$ of the symmetric matrix can be given as

$$(\mathbf{K}_{R_2})_{n_2,n_2'} = \langle \chi_{n_2}(R_2) | \frac{\partial^2}{\partial R_2^2} | \chi_{n_2'}(R_2) \rangle$$

$$= -\frac{1}{2}(n_2(n_2+1)+1)\delta_{n_2,n_2'}$$

$$+ \frac{1}{4}(n_2+1)(n_2+2)\delta_{n_2+2,n_2'}. \tag{14}$$

It is important to note that if the same number of orthogonal and nonorthogonal basis functions are employed for setting up the eigensystem problem the computed eigenvalues are exactly the same. We also note that Baye *et al.*[16] employed similar basis sets, however, the matrix elements of the one-dimensional model Hamiltonians were given in a grid representation.

B. The kinetic energy matrix

Employing either (10) and (11) or (13) and (14) the matrix elements of the kinetic energy operator can be computed employing the following analytical formula:

$$(\mathbf{K})_{n_2l,n_2'l'} = -\frac{1}{2\mu_2}(\mathbf{K}_{R_2})_{n_2,n_2'}\delta_{l,l'}$$

$$+ \frac{1}{2\mu_1 R_1^2}(\mathbf{S})_{n_2,n_2'}l(l+1)\delta_{l,l'}$$

$$+ \frac{1}{2\mu_2}(\mathbf{R}_2^{-2})_{n_2,n_2'}l(l+1)\delta_{l,l'}. \tag{15}$$

In this equation matrix $\mathbf{S}$ is the unit matrix in the case of the orthogonal basis functions and is defined in (12) for the nonorthogonal basis set.

C. The potential energy matrix

The function $V^\pm(R_2,\Theta)$ can be written as

$$V^\pm(R_2,\Theta) = \sum_{i=0}^\infty \frac{R_<^i}{R_>^{i+1}} P_i(\mp\cos\Theta), \tag{16}$$

where $R_<$ ($R_>$) is the smaller (larger) $m_\pm R_1$ and R_2. The integral over the coordinate Θ is

$$V_{ll'}^\pm(R_2) = \langle P_l(\cos\Theta) | V^\pm(R_2,\Theta) | P_{l'}(\cos\Theta) \rangle$$

$$= \sum_{i=0}^\infty \frac{R_<^i}{R_>^{i+1}}(\mp 1)^i \langle P_l(\cos\Theta) | P_i(\cos\Theta) | P_{l'}(\cos\Theta) \rangle$$

$$= \sum_{i=|l-l'|}^{l+l'} \frac{R_<^i}{R_>^{i+1}}(\mp 1)^i c_i^{ll'}, \tag{17}$$

where[25]

$$c_i^{ll'} = \langle P_l(\cos\Theta) | P_i(\cos\Theta) | P_{l'}(\cos\Theta) \rangle$$

$$= \sqrt{(2l+1)(2l'+1)} \begin{pmatrix} l & i & l' \\ 0 & 0 & 0 \end{pmatrix}^2$$

$$\text{and } |l-l'| \leq i \leq l+l'. \tag{18}$$

Although the series in (16) has an infinite number of

terms, the integral of three Legendre polynomials is zero if $i < |l-l'|$ or $i > l+l'$. Therefore, only a finite number of terms have to be summed during the computation of the matrix elements of $V^\pm(R_2,\Theta)$. Since the integral of three Legendre polynomials is zero if $l+i+l'$ is odd, during evaluation of the final sum in Eq. (17) only every other i must be considered.

Using (18) one can set up the matrix representation of $V^\pm(R_2,\Theta)$ as

$$(\mathbf{V}^\pm)_{n_2l,n_2'l'}$$

$$= \langle \chi_{n_2}(R_2) | V_{ll'}^\pm(R_2) | \chi_{n_2'}(R_2) \rangle$$

$$= \sum_{i=|l-l'|}^{l+l'} c_i^{ll'}(\mp 1)^i \left(\int_0^{m_\pm R_1} \chi_{n_2}(R_2) \frac{R_2^i}{(m_\pm R_1)^{i+1}} \chi_{n_2'}(R_2) dR_2 \right.$$

$$\left. + \int_{m_\pm R_1}^\infty \chi_{n_2}(R_2) \frac{(m_\pm R_1)^i}{R_2^{i+1}} \chi_{n_2'}(R_2) dR_2 \right). \tag{19}$$

The required one-dimensional integrals can be calculated by numerical integration with arbitrary precision employing computer algebra, in the present case the MATHEMATICA program package.[26]

The matrix elements of the repulsion term corresponding to the two particles with m_2 and m_3 are simply

$$(\mathbf{V}_{23})_{n_2l,n_2'l'} = \frac{1}{R_1}(\mathbf{S})_{n_2,n_2'}\delta_{l,l'}, \tag{20}$$

where matrix $\mathbf{S}$ is the unit matrix in the case of the orthogonal basis functions and is defined in (12) for the nonorthogonal basis set.

D. The Hamiltonian matrix

The matrix representation of the final Hamiltonian matrix is given as

$$\mathbf{H} = \mathbf{K} + \mathbf{V}_{23} - \mathbf{V}^+ - \mathbf{V}^-. \tag{21}$$

When m_2 equals m_3 (e.g., in H_2^+ and D_2^+) both m_+ and m_- are $1/2$, and $m_\pm R_1$ equals $R_1/2$. The relation between $\mathbf{V}^+$ and $\mathbf{V}^-$ then becomes

$$(\mathbf{V}^+)_{n_2l,n_2'l'} = (\mathbf{V}^-)_{n_2l,n_2'l'} \quad \text{if } l+l' \text{ is even,}$$

$$(\mathbf{V}^+)_{n_2l,n_2'l'} = -(\mathbf{V}^-)_{n_2l,n_2'l'} \quad \text{if } l+l' \text{ is odd.} \tag{22}$$

All the matrix elements of $\mathbf{K}$ and $\mathbf{V}_{23}$ are zero when $l \neq l'$, and elements of $\mathbf{V}^+ + \mathbf{V}^-$ are also zero when $l+l'$ is odd [see Ref. 22]. Therefore, only cases when $l+l'$ is even result in nonzero matrix elements. This explains why the $\mathbf{H}$ matrix can be separated for an even and odd blocks, where both l and l' are even and odd, respectively. It means that one can build the Hamiltonian matrix using either the even or odd Legendre polynomials. The ground-state energy of H_2^+ and its symmetric isotopologs can be obtained by employing the even Legendre functions.

It is clear that after building either the even or odd blocks of the symmetric $\mathbf{H}$ matrix an eigenvalue problem has to be solved and the lowest eigenvalue is the requested energy level. The potential energy matrix will be the same for

TABLE I. Ground-state electronic energies, DBOCs, and AJCs for H_2^+, D_2^+, and HD^+ as a function of internuclear separation. The internuclear separations (R_1) are given in bohr. Complete basis set Born-Oppenheimer (BO) energies are in E_h. Diagonal Born-Oppenheimer corrections (DBOCs) and the adiabatic Jacobi corrections (AJCs) are given in cm^{-1}. The AJCs are differences between the results obtained from calculations using proper finite and infinite nuclear masses. All the AJCs are converged within the given precision. The AJCs were computed with basis sets (denoted as ($N_2\ L$), where N_2 and L are the number of R_2- and Θ-dependent basis functions, respectively) of (56 56), (56 56), (68 68), and (116 116) functions at 1, 2, 4, and 10 bohr internuclear separations, respectively. For H_2^+ and D_2^+ the employed variational parameters K of the radial basis functions (see text), are 32, 28, 28, and 38, in order. For HD^+ values of K were set to 32, 27, 27, and 40, in order. The nuclear masses employed for H and D are $1.007\,276\,47u$ and $2.013\,553\,21u$, respectively.

| R_1 | BO | H_2^+ | | D_2^+ | | HD^+ | |
		DBOC	AJC	DBOC	AJC	DBOC	AJC
1	−0.451 786	79.87	63.92	39.96	31.98	59.92	46.63
2	−0.602 635	56.87	44.54	28.45	22.28	42.66	32.71
4	−0.546 081	50.37	39.25	25.20	19.64	37.78	28.89
10	−0.500 577	59.48	49.22	29.76	24.63	44.62	[30.23][a]

[a]Not converged. The corresponding (92 92) and (104 104) results are 28.95 and 29.64 cm^{-1}, respectively.

both H_2^+ and D_2^+, therefore the most time consuming part of the calculation, i.e., computation of the potential energy matrix, does not need to be repeated when different masses are employed (e.g., mass of H or D). Furthermore, the kinetic energy matrix can also be easily recomputed by scaling the stored one-dimensional matrices with the new reduced masses [see Eq. (15)].

III. RESULTS AND DISCUSSION

Since our calculations are performed in a frame fixed in the molecule but with fixed values of R_1 we are free to vary the masses assigned to the nuclei. As we are not considering the rotational motions ($J=0$), if we were to allow the nuclear masses to increase without limit then our results would exactly match the traditional clamped nuclei calculation results to within computational accuracy. For comparison and to anchor our less traditional approach, accurate BO energies have been computed through conventional, nonrelativistic electronic structure computations. All energies are reported in hartree units $[E_h=m_e e^4/(4\pi\epsilon_0\hbar)^2]$ and all distances in bohrs ($a_0=4\pi\epsilon_0\hbar^2/m_e e^2$) based on the electron rest mass m_e and the elementary charge e.[27] All energy differences are given in cm^{-1}. Quoted energies include the nuclear repulsion energy, unless otherwise noted. In the case of a one-electron system, i.e., for H_2^+ and all of its symmetric and nonsymmetric isotopologs, the complete basis set (CBS) limit at the Hartree-Fock (HF) level yields the exact electron energies corresponding to the BO approximation.

In this study the conventional nonrelativistic BO and DBOC electronic structure computations have been performed with the program package PSI3,[28] with energies computed using the correlation-consistent (cc) aug-cc-pVNZ (N $=Q(4),5,6$) basis sets of Dunning.[29] The BO energies corresponding to the CBS limit have been obtained using a two-parameter[30] and a three-parameter[31] exponential extrapolation technique, where the extrapolated energies (E_{CBS}) are obtained as

$$E_{CBS} = E_{6Z} + \frac{E_{6Z} - E_{5Z}}{(6/7)\exp[9(\sqrt{6}-\sqrt{5})]-1} \quad (23)$$

and

$$E_{CBS} = \frac{E_{4Z}E_{6Z} - E_{5Z}^2}{E_{4Z} - 2E_{5Z} + E_{6Z}}, \quad (24)$$

respectively, and the E_{4Z}, E_{5Z}, and E_{6Z} energies are computed employing the aug-cc-pVQZ, aug-cc-pV5Z, and aug-cc-pV6Z basis sets, respectively. The two extrapolation formulas gave the same results within 0.3 cm^{-1}, the perhaps slightly more accurate[30] two-parameter results are reported in Table I as BO energies.

In a clamped nuclei calculation the only mass to consider is the electron mass. If the distances involved are expressed as multiples of a_*, where a_* is defined exactly as a_0 but with the actual mass m_{e*} of the unique particle used in the calculation, then the Hamiltonian operator can be scaled to produce a form in which there is no explicit reference to the mass. Thus the clamped nuclei form in Jacobi coordinates (3) can be written in terms of the scaled coordinates $\mathbf{t}_i^*$,

$$^\infty\hat{H}_{mol}^* = -\frac{1}{2}\nabla^2(\mathbf{t}_2^*)$$

$$+ \left(\frac{1}{|\mathbf{t}_1^*|} - \frac{1}{|\mathbf{t}_1^* d/(1+d) + \mathbf{t}_2^*|} - \frac{1}{|\mathbf{t}_1^*/(1+d) - \mathbf{t}_2^*|}\right). \quad (25)$$

The energy spectrum of this Hamiltonian for a fixed value of $D_1=|\mathbf{t}_1^*|$ will consist simply of numbers, $Q(D_1)$, and the required absolute energies are determined by multiplying these numbers by the atomic unit of energy E_* which is defined just as is E_h but using m_{e*} instead of m_e. Thus any particular eigenvalue represents an electronic state for an electron of mass m_{e*} at $R_1=D_1a_*$ and the same state for an electron of mass m_e but at $R_1=D_1a_0$. The clamped nuclei molecular Hamiltonian has essentially the same properties as an atomic Hamiltonian and thus Zhislin's result[32] holds and here, as for any positive ion, there are an infinite number of bound states whatever the electron mass is.

If R_1 is chosen to be 0 and so a united atom results, the scaling simply becomes

$$E^* = \frac{m_e^*}{m_e} E. \tag{26}$$

In general one has to consider scaling for distance as well as for energy. If an equilibrium internuclear distance D_{eq} is found for an energy Q_{eq} then

$$\frac{R_{eq}^*}{a_*} = \frac{R_{eq}}{a_0} \tag{27}$$

or

$$R_{eq}^* = \frac{m_e}{m_e^*} R_{eq}, \tag{28}$$

and at D_{eq} the energy scales as given in (26) if E^* and E correspond to R_{eq}^* and R_{eq}, respectively.

Because the general Jacobi coordinate Hamiltonian (3) contains two distinct masses it is not possible to use scaling arguments in quite the same way and so a computational exploration must be undertaken there and neither does Zhislin's result apply to its eigenvalues.

A. The effects of varying the nuclear mass (H_2^+, D_2^+, and HD$^+$)

In Table I, rotationless ($J=0$) ground-state electronic, adiabatic correction, and AJC energies are presented for the isotopologs H_2^+ (ppe), D_2^+ (dde), and HD$^+$ (pde) at fixed internuclear separations of $R_1 = 1$, 2, 4, and 10 bohrs, employing finite as well as infinite nuclear masses. These internuclear separations were selected for presentation as they represent a short, an almost equilibrium, an intermediate, and a long separation. The DBOC energies have been extrapolated with Eq. (23), the differences between the CBS and aug-cc-pV6Z HF DBOC results are less than 0.01 cm^{-1}. The so-called AJCs are defined as the difference between the results obtained from calculations using proper finite and infinite nuclear masses.

The variational Jacobi calculations employed basis sets that are denoted as (N_2 L), where N_2 and L are the number of R_2- and Θ-dependent basis functions, respectively. It is important to note that in the case of symmetric systems, e.g., H_2^+ and D_2^+, only the even block of **H** was built (see Sec. II D). Therefore, the dimension of the matrix, whose eigenvalue problem was solved, is $N_2 L/2$ (if L is even) instead of $N_2 L$. Preliminary computations at different internuclear separations and basis sizes established how the optimum value of the variational parameter of the radial basis functions, K (see Sec. II A), changes. K should be increased with decreasing R_1 and with an increase in the size of the radial basis. Optimal values of K have been chosen for the final computations. Due to the more compact and more spherically symmetric electron density in the cases of shorter internuclear separations the convergence behavior is better at R_1 which is smaller than the respective equilibrium value.

Since the potential energy matrix depends only on the relative masses of the two equally charged particles, see (4), for H_2^+ (and D_2^+) only the kinetic energy matrices were different when either infinite or finite masses were employed. The infinite nuclear masses were realized by neglecting the term involving $1/\mu_1$. The Jacobi calculation with infinite mass should converge, within computational accuracy, to the exact BO energy. At 1 bohr internuclear separation the extrapolated BO electronic energy of H_2^+ is $-0.451\,786\,E_h$. The difference between the Jacobi result and this BO value is about 1 μE_h when the basis set of (92 92) functions is used. It seems reasonable therefore to take the two distinct infinite nuclear mass formulations as corresponding to the same physical situation and to suppose that no ambiguity will arise in comparing calculated results between formulations. The AJCs converge much faster with basis size than the absolute energies, and even small basis sets [on the order of about (32 32) functions] reproduce the AJCs to better than 0.1 cm^{-1} at internuclear separations less than about 4 bohrs.

The infinite mass results for HD$^+$ are obtained from computations where $d = m_3/m_2$ is fixed at $m(D)/m(H)$, while both m_2 and m_3 go to infinity. This ensures that even for HD$^+$ the potential energy matrix is the same during computations with finite and infinite masses.

It is possible to set only one of the nuclear masses to infinity during the variational Jacobi calculations while the other mass has its proper finite value. This way the center of mass of the two nuclei is shifted into the nucleus having infinite mass. (Relevant plots of the wave functions of this molecular ion, denoted as $^\infty$HH$^+$, are given in Figs. 3 and 5).

The AJCs for H_2^+ and D_2^+ given in Table I are converged to within 0.01 cm^{-1}. The AJCs given in Table I for HD$^+$ are converged to a similar accuracy, except at 10 bohrs. These AJCs were computed with basis sets of (56 56), (56 56), (68 68), and (116 116) functions at 1, 2, 4, and 10 bohr internuclear separations, respectively.

Neither the DBOCs nor the AJCs involve the repulsion term $1/R_1$, and so both are expected to move smoothly to a united atom limit as R_1 tends to 0. For example, the AJCs of H_2^+ are 116.19, 119.45, and 119.50 cm^{-1} at 0.1, 0.01, and 0.001 bohr internuclear separations, respectively (the exact united atom limit is 119.50 cm^{-1}).

The general relation for the DBOC energy of an isotopolog AB is

$$E_{DBOC}(AB; R_1) = \frac{1}{m_A} F_A(R_1) + \frac{1}{m_B} F_B(R_1), \tag{29}$$

where m_A and m_B are the masses of nuclei A and B, and F_A and F_B are the related atomic (isotope-independent) correction functions. Therefore, the DBOCs of the different isotopologs of H_2^+ can be obtained at all internuclear separations from the DBOC of H_2^+ using a simple scaling with the nuclear masses as

$$E_{DBOC}(D_2^+) = \frac{m_p}{m_d} E_{DBOC}(H_2^+) \tag{30}$$
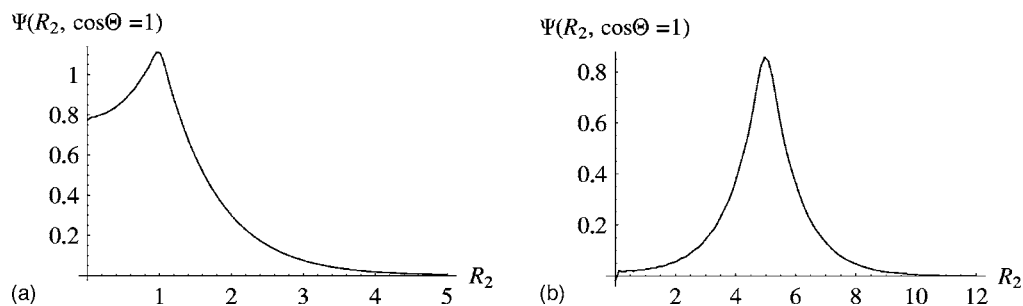
and

FIG. 1. Wave functions $\Psi(R_2, \cos\Theta = 1)$ of H_2^+ at $R_1 = 2$ bohrs (left) and $R_1 = 10$ bohrs (right), using proper finite masses for all three particles and a basis of (44 44) functions (the variational parameter K has been set to 23 and 15 for left and right plots, respectively).

$$E_{\text{DBOC}}(\text{HD}^+) = \frac{1}{2}\left(1 + \frac{m_p}{m_d}\right) E_{\text{DBOC}}(\text{H}_2^+). \qquad (31)$$

Since the mass of the proton, m_p, is almost half of the mass of the deuteron, m_d, the DBOC of D_2^+ and HD^+ is almost exactly 50% and 75% of the DBOC of H_2^+, respectively. However, the picture is not this simple for the AJCs, as the AJCs of D_2^+ and HD^+ cannot be obtained by scaling the AJC of H_2^+. Therefore, it is important to note that the AJCs of D_2^+ are about half of the AJCs of H_2^+, similar to the DBOCs. On the other hand, the AJCs of HD^+ are not 75% of the AJCs of H_2^+ and the proportions do depend on the internuclear separations. The AJCs of HD^+ are about 73% of the AJCs of H_2^+ at 1, 2, and 4 bohrs. There is otherwise no obvious relationship between the DBOC and the AJC. Because the DBOC is uniformly larger in magnitude than the AJC it must be assumed to correct the BO approximation for more than simply the translational motion.

B. Wave functions

One-dimensional (1D) plots of the two-dimensional (2D) wave functions, $\Psi(R_2, \cos\Theta)$, are given in Fig. 1–6, where the Jacobi angle is fixed at either $0°(\cos\Theta = 1)$ or $180°(\cos\Theta = -1)$. In the case of H_2^+ and D_2^+, the wave functions are symmetric with respect to $\cos\Theta$, i.e., $\Psi(R_2, 1) = \Psi(R_2, -1)$, and the cusp is at $R_1/2$.

For the nonsymmetric isotopologs HD^+ and $^\infty HH^+$, let us consider first the wave function at $R_1 = 2$ bohrs. In the case of HD^+, the nuclear positions correspond to m_+R_1 and m_-R_1 if the wave functions are $\Psi(R_2, 1)$ and $\Psi(R_2, -1)$, respectively. Therefore, the cusps are at m_+R_1 and m_-R_1. As to $^\infty HH^+$, the origin of R_2 in the proton having infinite mass, therefore,

$\Psi(R_2, -1)$ has a cusp at $R_2 = 0$, and the peak of $\Psi(R_2, 1)$ is at $R_2 = R_1$. Even at the internuclear separation of 2 bohrs the asymmetry can be recognized in the wave functions, namely, the peaks are a little bit higher at the positions of the heavier nuclei. If a much longer internuclear distance is considered (see figures with $R_1 = 10$ bohrs), one can see that the electron density will be much larger around the heavier nucleus (D or $^\infty H$).

C. Expectation values

Expectation values of the proton-electron distance and the deuteron-electron distance for H_2^+ and its isotopologs have been computed at different fixed internuclear separations.

At short internuclear separation the average p-e distance equals the d-e distance within numerical precision. However, upon increasing the nuclear separation the proton-electron distance is getting longer than the deuteron-electron distance. For example, at $R_1 = 1$ bohr both the p-e and d-e average distances are 1.138 bohr, while at $R_1 = 4$ bohrs a small difference between the expectation values can be observed, since the p-e and d-e distances are 2.720 and 2.715 bohrs, respectively. Note that the convergence of the expectation values is excellent at short internuclear separations and becomes worse with the increase of R_1.

Next, let us consider the average p-e and d-e distances at long internuclear separations. HD^+ dissociates to $H^+ + D$, while the $H + D^+$ dissociation channel is less preferred.[33] This is not surprising since the energy of the separated D atom is a bit lower than that of the H atom, though traditional clamped nuclei electronic structure theories cannot deal with this charge asymmetry in HD^+. Our method is able to follow
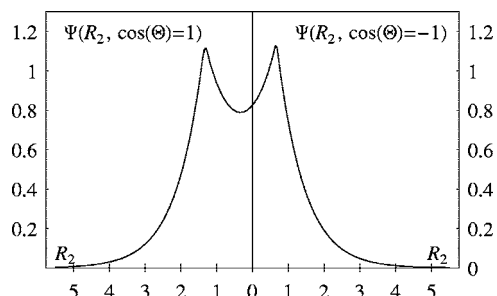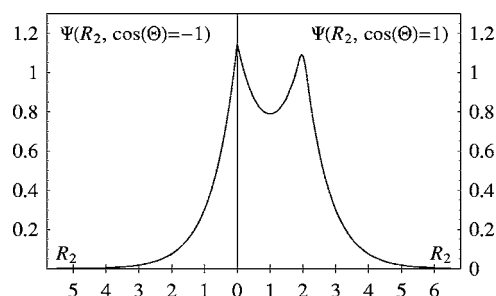

FIG. 2. Wave function $\Psi(R_2, \cos\Theta)$ of HD^+ at $R_1 = 2$ bohr internuclear separation using proper finite masses for all three particles and a basis of (56 56) functions (the variational parameter K has been set to 27).

FIG. 3. Wave function $\Psi(R_2, \cos\Theta)$ of $^\infty HH^+$ at $R_1 = 2$ bohr internuclear separation using infinite mass for $^\infty H$ and proper finite mass for H and a basis of (44 44) functions (the variational parameter K has been set to 23).
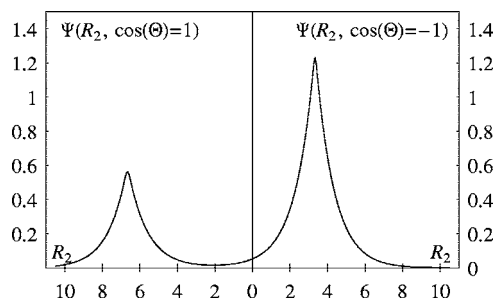
FIG. 4. Wave function $\Psi(R_2, \cos\Theta)$ of HD$^+$ at $R_1 = 10$ bohr internuclear separation using proper finite masses for all three particles and a basis of (116 116) functions (the variational parameter K has been set to 40). Note that the AJC is not converged with this basis (Table I).

FIG. 5. Wave function $\Psi(R_2, \cos\Theta)$ of at $R_1 = 10$ bohr internuclear separation using infinite mass for ^{2}H and proper finite mass for H and a basis of (44 44) functions (the variational parameter K has been set to 8). Note that the wave function is not converged with this basis.

this symmetry breaking. At 10 bohr nuclear separation the p-e average distance is 8.5 bohrs, while the d-e distance is only 3.1 bohrs [with a basis of (116 116) functions]. This means that the electron is localized near to the deuteron, which can also be seen from the wave function of Fig. 4.

In 2005 Bubin *et al.*[24] published a theoretical study where the full nonadiabatic problem of HD$^+$ was solved variationally, and the expectation values of d-p, p-e, and d-e distances for the $J=0$ vibrational levels of HD$^+$ were computed. We can compare the average distances obtained from the present approach to the nonadiabatic ones if the fixed R_1 distance in the Jacobi method is set to the expectation value of the d-p distance corresponding to one of the vibrational states. For example, considering the ground vibrational state, the nonadiabatic calculation provided 2.055 bohrs for the d-p distance and 1.688 bohrs for both the p-e and d-e distances. If the fixed internuclear distance is set to 2.055 bohrs, the same 1.688 bohr values are obtained for the nucleus-electron distances in our 2D treatment as in the full three-dimensional treatment.[24] This proves the utility of the adiabatic Jacobi approach at small internuclear separations. As to longer d-p separations, for example, 6.227 bohrs corresponding to the $v=18$ vibrational level, the full nonadiabatic calculation showed some asymmetry of the electron distribution since the p-e average distance is 3.91 bohrs, while the d-e distance is only 3.82 bohrs. At fixed internuclear separation of 6.227 bohrs the present method provides 3.90 and 3.85 bohrs for the p-e and d-e average distances, respectively. Therefore, the present method is able to provide an almost quantitative way to deal with the asymmetry in HD$^+$ and demonstrates a breakdown of the BO approximation.
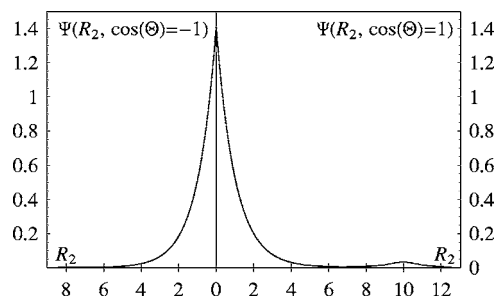
D. Varying the masses and the charges

The present method investigated allows change in (a) the value of the electron rest mass, (b) the mass of the unique particle (electron), (c) the value of the elementary charge, and (d) the charge of the unique particle (electron). In the case of (a) both m_p and m_e are changed, while m_p/m_e remains 1836.15. Similarly, in the case of (c) both p and e have the same nonunit charge with opposite sign.

For case (b) numerical results are presented in Table II for those counterfactual three-particle systems, (ppe^*), which contain two protons having either infinite or finite masses and one particle with unit negative charge having different masses from $0.1m_e$ to $10m_e$. These energies were obtained at different internuclear separations of the two positive charges. In the case of infinite nuclear masses (a) and (b) provide, of course, the same results. All the computations have been performed using a basis of (32 32) functions, and K has been optimized for each basis and internuclear separation. The optimal value of K increases linearly with the mass of the negatively charged particle.

Considering the energies in cases (a) and (b), corresponding to infinite nuclear masses, the following exact formula holds

$$E_{ppe^*}(R_1) = \frac{m_{e^*}}{m_e} E_{ppe}\left(\frac{m_{e^*}}{m_e} R_1\right). \tag{32}$$

This relation implies that the equilibrium distances of the (ppe^*) systems scale with m_e/m_{e^*}, therefore,
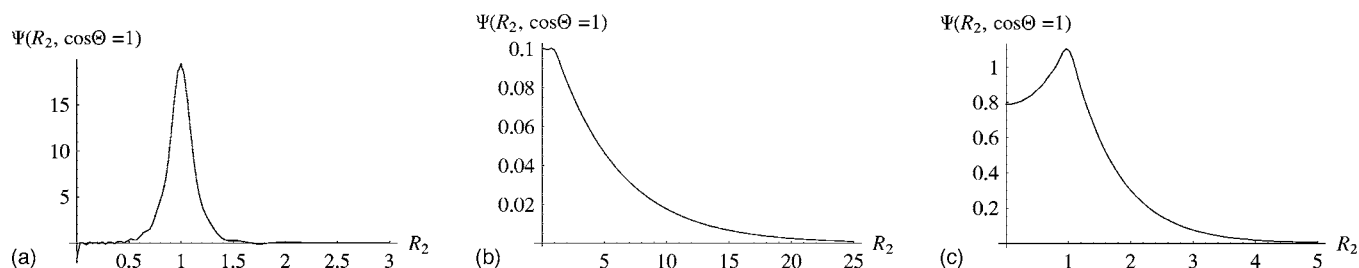

FIG. 6. Wave functions $\Psi(R_2, \cos\Theta = 1)$ of (ppe^*) at $R_1 = 2$ bohr internuclear separation using proper finite masses for the protons and different masses for the negatively charged particle e^*, namely, $m_{e^*} = 10m_e$, $m_{e^*} = 0.1m_e$, and $m_{e^*} = m_e$ for the left, middle, and right plots, respectively. A basis of (32 32) functions (with the variational parameter K set to 60, 2, and 19 for the left, middle, and right plots, respectively) has been used.

TABLE II. Dependence of energies and their AJC corrections for the (ppe^*) systems on the mass of e^*. The masses of e^* are given in a.u. The internuclear separations (R_1) are given in bohr. The incomplete basis Jacobi energies with infinite masses (Inf. mass) are in E_h, while the adiabatic Jacobi corrections (AJCs) are given in cm^{-1}. The AJCs are differences between the results obtained from calculations using proper finite and infinite nuclear masses. All the computations have been performed using a basis of (32 32) functions, and the variational parameter K of the radial basis functions (see text) has been optimized for each basis and internuclear separations. The nuclear mass employed for p is $1.007\,276\,47u$.

$m_{e^*}=0.1$			$m_{e^*}=0.5$			$m_{e^*}=1$			$m_{e^*}=2$			$m_{e^*}=10$		
R_1	Inf. mass	AJC	R_1	Inf. mass	AJC	R_1	Inf. mass	AJC	R_1	Inf. mass	AJC	R_1	Inf. mass	AJC
10	−0.045 18	0.639	2	−0.2259	16.0	1	−0.4518	63.9	0.5	−0.9035	256	0.1	−4.518	6370
20	−0.060 26	0.445	4	−0.3013	11.1	2	−0.6026	44.5	1	−1.205	178	0.2	−6.026	4440
40	−0.054 58	0.392	8	−0.2729	9.79	4	−0.5458	39.2	2	−1.092	157	0.4	−5.458	3900

$$R_{eq}(ppe^*) = \frac{m_e}{m_{e^*}} R_{eq}(ppe). \quad (33)$$

As to the AJCs, in case (a) the following exact relation holds

$$E_{ppe^*}^{AJC}(R_1) = \left(\frac{m_{e^*}}{m_e}\right)^2 E_{ppe}^{AJC}\left(\frac{m_{e^*}}{m_e}R_1\right). \quad (34)$$

The numerical results given in Table II show that in case (b) Eq. (34) remains an excellent approximation if $m_{e^*} \ll m_p$. Two numerical examples follow. At 1 bohr intenuclear separation the AJC corresponding to the proper mass of the electron is 63.9 cm^{-1}. If m_{e^*} is $0.1m_e$, the AJC at a 10 bohr internuclear separation is 0.639 cm^{-1}, while in the case of $m_{e^*}=10m_e$, the AJC is 6370 cm^{-1} at a 0.1 bohr distance.

On Fig. 6 1D cuts of the wave functions are shown, where the distance of the two protons is fixed at 2 bohrs and the mass of the particle carrying the negative charge is increased and decreased by one order of magnitude. This fixed internuclear separation corresponds closely to the equilibrium distance for (ppe), therefore, 2 bohrs is a dissociative distance if the mass of e^* is ten times larger than the proper mass of e, and this distance is much shorter than the equilibrium distance of (ppe^*) if $m_{e^*}=0.1m_e$. These are the reasons why the wave function is localized near the proton when the mass of the negatively charged particle is huge, i.e., ten times larger than the proper mass of the electron, and the density halfway between the two protons is exceedingly small.

In case (c) the following exact formulas hold:

$$E_{pp\tilde{e}}(R_1) = \left(\frac{q_{\tilde{e}}}{q_e}\right)^4 E_{ppe}\left(\left(\frac{q_{\tilde{e}}}{q_e}\right)^2 R_1\right) \quad (35)$$

and

$$E_{pp\tilde{e}}^{AJC}(R_1) = \left(\frac{q_{\tilde{e}}}{q_e}\right)^4 E_{ppe}^{AJC}\left(\left(\frac{q_{\tilde{e}}}{q_e}\right)^2 R_1\right), \quad (36)$$

where q refers to the charge of the particle and $\tilde{e}$ refers to an electron with a nonunit charge.

In case (d) the AJCs scale as

$$E_{pp\tilde{e}}^{AJC}(R_1) = \left(\frac{q_{\tilde{e}}}{q_e}\right)^2 E_{ppe}^{AJC}\left(\frac{q_{\tilde{e}}}{q_e}R_1\right), \quad (37)$$

while in the case of infinite nuclear masses no relation was found for the energies which include the nuclear repulsion energy. However, the following exact formula:

$$E_{pp\tilde{e}}^{el}(R_1) = \left(\frac{q_{\tilde{e}}}{q_e}\right)^2 E_{ppe}^{el}\left(\frac{q_{\tilde{e}}}{q_e}R_1\right) \quad (38)$$

holds for the electronic energy when the constant energy of the nuclear repulsion is neglected.

Since the AJCs scale with the square of m_{e^*}/m_e, while the energies scale linearly, the decrease of the electron rest mass provides relatively smaller and smaller AJCs. More importantly, the increase of either the electron rest mass or m_{e^*} means an increase in the breakdown of the BO approximation. The picture is different in the case of changing the elementary charge. Due to the same scaling in the total energies corresponding to infinite nuclear masses and in the AJCs, the BO approximation is not compromised by the increase of the elementary charge.

IV. CONCLUSIONS

In traditional electronic structure computations for the determination of molecular structure of usual chemical systems, the relatively heavy nuclei are clamped to yield a particular nuclear geometry, and an approximate solution of the electronic problem specified by the clamped nuclei Schrödinger Coulomb Hamiltonian yields an electronic energy. The sum of this energy and the classical nuclear repulsion energy is believed to represent, to a good first approximation, the total energy of the molecule at this configuration. Because the clamped nuclei Hamiltonian involves only one mass, the notional electronic mass, this mass can be incorporated into the coordinates to define a new unit of length and the mass simply becomes the unit, in much the same way as discussed in forming the infinite nuclear mass Hamiltonian [Eq. (25)]. Thus, just like the solutions of Eq. (25), solutions to the clamped nuclei problem depend neither upon the mass of the nuclei nor that of the electron, and they can be scaled to whatever value is implied by a particular choice of the unit mass. To compare the results of such simplified calculations with observation, it is sensible to use an "experimental" value of the electron mass to assign the results.

However, what is known about solutions of the full molecular structure problem, usually called the nonadiabatic approach, shows that whether or not stable molecular solutions to the full Schrödinger Coulomb Hamiltonian exist, depends crucially on the ratios of the nuclear to the electronic masses. As we have argued here, it is not safe to attempt to make the nuclear masses infinite in a nonadiabatic calculation in the hope of achieving a clamped nucleus result, but it is perfectly

safe to work in a formulation in which the nuclei can be clamped and at the same time to allow the nuclear masses to vary. Such a formulation has been developed here. It allows the exact separation of not only the translational but also the rotational motion from the vibrational problem.

It has been established that when the nuclear masses are taken as infinite in the nonadiabatic electronic structure problem of the three unit charge system, with the distance between the same charges kept fixed, then it is precisely equivalent to a standard clamped nuclei calculation. The adiabatic Jacobi corrections (AJCs), defined as the difference in the energies obtained with finite and infinite nuclear masses, are not equivalent with the diagonal Born-Oppenheimer corrections (DBOC) from clamped nuclei calculations, except in the united atom case. This is due to the different Hamiltonians used in the two formulations. At all internuclear distances the AJC correction is substantially smaller than the DBOC correction, being usually about 4/5 of it.

This observation leaves open the question of whether or not it would be more "correct" to calculate a potential curve for a diatomic molecule using the Jacobi formulation with proper finite masses or by a standard electronic structure method and adding only the DBOC or even nonadiabatic corrections developed by Bunker and Moss.[19] On balance we would suggest that the Jacobi approach is the correct one since the relationship of the clamped nuclei (but proper mass) calculations to the full problem is precisely formulated. This is not the case for the standard clamped nuclei approach where the relationship of the translationally invariant coordinates and the internal coordinates and Eulerian angles to the laboratory fixed coordinates is not explicitly formulated, even though it is essential to make such coordinate choices in order to perform calculations on the internal motion of the molecule. Usually a harmonic-oscillator-rigid-rotor model is used with the internuclear distance and potential calculated using the clamped nuclei Hamiltonian. But it is not clear that the relevant nuclear motion problem in this context should be a harmonic oscillator and a rigid rotor. These problems are discussed in Sec. VII of Ref. 34. We think that our suggestion that the Jacobi approach is the correct one is also supported by the calculated interparticle expectation values which match the fully nonadiabatic results of Bubin *et al.* on the HD$^+$ system[24] to the expected accuracy.

Should our suggestion about the approach in the present case actually prove to be correct, then an associated suggestion is that it would, in general, be better to approach all clamped nuclei calculations in terms of a formulation in which the nuclei could be clamped, but proper masses could be used. There are of course many problems involved in actually doing this, not least because of the difficulty of finding suitable sets of translationally invariant coordinates and subsequently Eulerian angles and internal coordinates. But

should it be wished to consider more generally counterfactual systems such as we have considered in Sec. III D here, then there is no alternative but to work using these. The literature about such coordinate choices is extensive and varied. Such matters are also considered in the cited review.[34]

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