Brief Reports

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Adiabatic hyperspherical treatment of the H_2^+ molecule

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The simplest molecule is treated theoretically using hyperspherical coordinates. It is argued, and demonstrated semiquantitatively, that the adiabatic body-frame approximation in hyperspherical coordinates is nearly identical to the Born-Oppenheimer approximation.

Significant progress toward an understanding of two-electron correlations in atoms has resulted from an adiabatic treatment of the Schrödinger equation in hyperspherical coordinates.[1–7] This adiabatic approach begins by replacing the six coordinates of the two electrons $(\vec{r}_1, \vec{r}_2)$ by a hyperspherical radius $R=(r_1^2+r_2^2)^{1/2}$ and some choice of five angular coordinates Ω. This choice of a collective radius R generalizes readily to any number of particles with arbitrary masses m_i, as emphasized by Smirnov and Shitikova[8] and by Fano[9]:

$$R^2=\sum m_i r_i^2/M \ , \tag{1}$$

where r_i is the distance between the ith particle and the center of mass. Here the choice of the proportionality constant M is not crucial, but usually it is taken to be the total mass of all particles. It is important that R^2 be proportional to the total moment of inertia of all particles,[9] as the kinetic energy operator is separable for this choice only.

The success of Refs. 1–7 in treating adiabatically the evolution in R of a doubly excited wave function has been remarkable at low energies, despite the absence of any obvious physical justification for the observed adiabaticity. In the more familiar context of diatomic molecules, an adiabatic treatment of the nuclear coordinates is justified by the observation that electron velocities are typically much larger than nuclear velocities.[10] It should be instructive, therefore, to compare the adiabatic hyperspherical treatment of H_2^+ with the more familiar Born-Oppenheimer treatment.[11] This comparison is the purpose of this Brief Report. The main conclusion, to be amplified below, is that these two approximations are very nearly identical. A qualitative analysis, coupled with an exploratory calculation, points to this result. In view of our relatively fragmentary experience with the hyperspherical method to date, this agreement is reassuring and lends credence to the use of adiabatic hyperspherical treatments in other contexts.[12–15]

To begin with, consider an electron in the field of two protons separated by a distance r_N. (Atomic units will be used throughout.) As a simplifying approximation, the molecular center of mass will be taken as a purely *nuclear* center of mass, which is the midpoint between the nuclei. In this frame the Schrödinger equation is

$$\left[-\frac{1}{2\mu}\frac{\partial^2}{\partial r_N^2}-\frac{1}{2}\frac{\partial^2}{\partial r^2}+\frac{\vec{l}_N^{\,2}}{2\mu r_N^2}+\frac{\vec{l}^{\,2}}{2r^2}+V(\vec{r},\vec{r}_N)-E\right]\psi=0 . \tag{2}$$

In Eq. (2), $\mu=M/2$ is the nuclear reduced mass, r is the distance of the electron from the nuclear center of mass, while $\vec{l}_N^{\,2}$ and $\vec{l}^{\,2}$ are the squared angular momenta of the nuclei and of the electron, respectively. Moreover, a factor rr_N has been extracted from the wave function to eliminate first-derivative terms in the kinetic energy operator. It is convenient to introduce a rescaled radial variable

$$\xi=r/\gamma \tag{3}$$

in which the dimensionless parameter γ is defined by

$$\gamma=(\mu/m_e)^{1/2}=\mu^{1/2}(\text{a.u.}) \ . \tag{4}$$

This brings the H_2^+ Schrödinger equation into the form

$$\left[\frac{-1}{2\mu}\left(\frac{\partial^2}{\partial r_N^2}+\frac{\partial^2}{\partial \xi^2}-\frac{\vec{l}_N^{\,2}}{r_N^2}-\frac{\vec{l}^{\,2}}{\xi^2}\right)+V-E\right]\psi=0 \ . \tag{5}$$

The transformation to hyperspherical coordinates can

now be performed using the usual two-dimensional transformation from Cartesian coordinates to polar coordinates. The coordinates to be used in place of (r_N, ξ) are then

$$R^2=r_N^2+\xi^2=r_N^2+\frac{2}{M}r^2;\ \alpha=\tan^{-1}\left(\frac{\xi}{r_N}\right). \tag{6}$$

The Schrödinger equation now takes the form

$$\left(-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2}-\frac{1}{8\mu R^2}+\hat{U}(R,\Omega)-E\right)\Psi=0\ , \tag{7}$$

where the operator $\hat{U}$ is given by

$$U(R,\Omega)=-\frac{1}{2\mu R^2}\left(\frac{\partial^2}{\partial\alpha^2}-\frac{\vec{l}_N^{\,2}}{\cos^2\alpha}-\frac{\vec{l}^{\,2}}{\sin^2\alpha}\right)+V(R,\Omega)\ , \tag{8}$$
$$\Psi=R^{1/2}\psi\ .$$

The qualitative properties of this equation are readily apparent. Observe that the potential V is attractive only for $r\lesssim r_N$. For larger electronic radii r the Coulomb repulsion overwhelms the electron-nuclear attraction. As a result the wave function will usually be confined to very small values of $\alpha=\tan^{-1}(r/\gamma r_N)$, namely,

$$\alpha\lesssim\mu^{-1/2}=0.0330\ \text{rad}\ . \tag{9}$$

Notice also that for this range $r\lesssim r_N$, the hyperspherical radius R is nearly identical to the internuclear distance r_N, to within small terms of order m_e/M. To this same level of approximation the electron radius is $r\approx\mu^{1/2}R\,\alpha$. From this discussion alone it is apparent that the Born-Oppenheimer potential curves (eigenvalues of $H_{r_N=\text{const}}$) should be nearly identical to the hyperspherical potential curves [eigenvalues of $\hat{U}(R,\Omega)=H_{R=\text{const}}$].

A more detailed comparison of these two approaches requires the solution of

$$\hat{U}(R,\Omega)\phi_\mu(R;\Omega)=U_\mu(R)\phi_\mu(R;\Omega)\ . \tag{10}$$

The nuclear rotation term in Eq. (8) is sufficiently small at small α that it is sensible to exclude it from the initial calculation of potential curves, with the intention of including it perturbatively at some later stage. This is accomplished by diagonalizing, instead of $\hat{U}(R,\Omega)$, the operator

$$\hat{U}^{(0)}(R,\Omega)=\hat{U}(R,\Omega)-\vec{l}_N^{\,2}/(2\mu R^2\cos^2\alpha)\ . \tag{11}$$

Physically this implies that the eigenvalues $U_\mu^{(0)}(R)$ of $\hat{U}^{(0)}$ can be interpreted as "body-frame" potential curves. In keeping with this point of view, the internuclear axis $\hat{r}_N$ will be adopted as the z axis in the body frame.

The potential energy then has the form

$$V=\frac{1}{r_N}-\frac{1}{|\vec{r}-\frac{1}{2}r_N\hat{z}|}-\frac{1}{|\vec{r}+\frac{1}{2}r_N\hat{z}|}\ . \tag{12}$$

One method for solving for $U_\mu^{(0)}(R)$ starts from the single-center expansion

$$\phi_\mu^{(0)}(R;\Omega)=\sum_{l=0}^{\infty}Y_{l\Lambda}(\hat{r})g_\mu^{l\Lambda}(R;\alpha)\ . \tag{13}$$

This leads to an infinite set of coupled differential equations in α for the $g_\mu^{l\Lambda}$, subject to the boundary conditions that each $g_\mu^{l\Lambda}$ vanishes at $\alpha=0,\ \frac{1}{2}\pi$. These coupled equations can be solved by direct numerical integration, as described in Refs. 1 and 5.

Figure 1 shows the lowest adiabatic hyperspherical potential curve obtained numerically by retaining either the lowest two even parity terms in (13) ($l=0,2$) or the lowest four such terms ($l=0,2,4,6$). Also shown for comparison is the usual Born-Oppenheimer potential curve for the H_2^+ ground state.[16] The main result to notice is that for $R\lesssim 1$ Å, where the truncated single-center expansion is expected to be realistic, *the hyperspherical potential curve is almost identical to the Born-Oppenheimer potential curve.* As R increases, of course, the single-center expansion requires a very large number of terms if it is to be realistic. This is the reason that the single-center results deviate increasingly from the Born-Oppenheimer results as R increases. Nonetheless, these fragmentary calculations support the conclusion that the hyperspherical and Born-Oppenheimer adiabatic potential curves are very nearly the same.

It should be pointed out that exploratory calculations of the H_2^+ ground-state energy have been previously attempted by Whitten and Sims,[17] without reliance on either an adiabatic or a body-frame approximation. They experienced convergence difficulties and reported no results because their basis set was

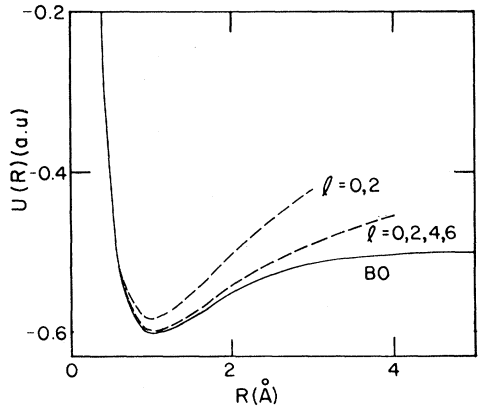

FIG. 1. Adiabatic potential curves for the ground state of H_2^+. The smooth curve is the Born-Oppenheimer (BO) potential curve from Ref. 16. The two dashed curves are the approximate hyperspherical results obtained using a single-center expansion in the body frame which retains either the lowest two terms or the lowest four terms in Eq. (13).

poorly suited to three-body systems with greatly differing masses.[17] The present coupled differential equation approach is expected to bypass this problem to some extent, although it does suffer from slow convergence at large R. The recently developed approach to three-body systems by Mignaco and Roditi,[18] using a hyperspherical harmonic expansion, should suffer from severe convergence difficulties analogous to those mentioned in Ref. 17, simply because it takes extremely high-order harmonics to confine the wave function within small $\alpha \lesssim \mu^{-1/2}$.

At *very* small radii, the two approaches differ considerably. In this range the electronic orbital angular momentum $\vec{l}$ is a good quantum number, and the hyperspherical potential curves assume the limiting form

$$U_\mu^{(0)}(R) \underset{R\to 0}{\to} \frac{(l+2m_\mu+2)^2}{2\mu R^2}+\frac{c_\mu}{R}+\cdots , \qquad (14)$$

in which m_μ is the number of nodes in α of $g_\mu^{l\Lambda}(R;\alpha)$.

The presence of this R^{-2} repulsion at small radii is typical of hyperspherical studies. It represents a generalized angular momentum barrier[19,20] associated with the kinetic energy in the radial correlation coordinate α and in the angular correlation coordinate $\hat{r}\cdot\hat{z}$. No analog of this kinetic energy term is present in the Born-Oppenheimer potential curves, since the nuclei are literally frozen in space, and accordingly the Coulomb repulsion $1/R$ is the leading term at small radii. The coefficient c_μ in Eq. (14) is the average of the Coulomb potential over Ω (at $R=1$ a.u.) using the appropriate adiabatic wave function $\phi_\mu(R;\Omega)$. It is worth stressing, however, that the small-R form (14) is applicable only for very small radii $R \lesssim \mu^{-1/2}$, and thus its deviation from the Born-Oppenheimer potentials is not apparent over the usual range of nuclear vibrations.

At large R instead, each of the hyperspherical potential curves $U_\mu^{(0)}(R)$ converges to a hydrogen energy level,

$$U_\mu^{(0)}(R) \underset{R\to\infty}{\to} -1/n^2+O(R^{-2}) . \qquad (15)$$

The large-R discrepancy between the hyperspherical and Born-Oppenheimer potential curves decays as R^{-2}. This discrepancy is discussed in another context in the Appendix of Ref. 1, and it is largely canceled when the nonadiabatic correction term $-(\phi_\mu|\partial^2\phi_\mu/\partial R^2)$ is added to the potential.

Owing to the limited accuracy of the present numerical results, particularly at large R, it is impossible to compare the hyperspherical and Born-Oppenheimer adiabatic approximations quantitatively. This task will be left for future studies.

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