

## Vibrational–rotational ( $\nu$ – $J$ ) levels of $\text{HD}^+$ , evaluated in the adiabatic approximation for the electronic ground state ( $1s\sigma_g$ )

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**Abstract.** The vibrational–rotational ( $\nu$ – $J$ ) energies of  $\text{HD}^+$  in the electronic ground state ( $1s\sigma_g$ ) are calculated in the ‘adiabatic’ approximation. The accurate wave functions and energies calculated in the approximation, where the nuclei are ‘infinitely heavy’, are used as the basis for the calculation, and thus the ( $\nu$ – $J$ ) energies are believed to be better. Furthermore, meticulous attention has been paid to the numerical evaluation of the ( $\nu$ – $J$ ) energies, ensuring that the possible numerical truncations, at each stage, are reduced to a minimum, thus enhancing the credence that the energy eigenvalues within the limits of the approximation, are better than the ones reported earlier.

**Keywords.** Born–Oppenheimer approximation; adiabatic approximation; nonadiabatic approximation; clamped nuclei; infinitely heavy nuclei.

### 1. Introduction

The charge asymmetry in the  $\text{HD}^+$  molecule makes it possible to observe the vibrational–rotational spectrum as an infrared spectrum as opposed to only a Raman spectrum for the  $\text{H}_2$  molecule (Herzberg 1966). This permits observation of the vibrational–rotational frequencies with much greater accuracy, thereby enabling one to obtain the vibrational–rotational energy eigenvalues ( $\nu$ ,  $J$ ) of the  $\text{HD}^+$  molecule with great precision (Wing *et al* 1976; Spezeski 1977). We recently calculated (Bhattacharjee *et al* 1983) *extremely precise* energy eigenvalues and eigenfunctions of the three-body quantum mechanical problem. It is well known (Born and Oppenheimer 1927) that these wave-functions can be used as a basis for studying the nuclear motion in the  $\text{H}_2^+$  or the  $\text{HD}^+$  molecule in a series of successive approximations, viz, the Born–Oppenheimer (BO) approximation, the adiabatic approximation and the non-adiabatic approximation. The present paper is an attempt to compute the  $\nu$ – $J$  energy levels of the  $\text{HD}^+$  molecule in the BO and the adiabatic approximations using the static wave functions of the  $\text{HD}^+$  molecule (the nuclei being infinitely heavy) obtained in our earlier paper (Bhattacharjee *et al* 1983).

Hunter and Pritchard (1967) had obtained the ( $\nu$ ,  $J$ ) levels in the electronic ground state ( $1s\sigma_g$ ) for the  $\text{HD}^+$  molecule, both in the adiabatic and the non-adiabatic approximations. Comparison with the experimental results of Wing

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*et al* (1977) yielded excellent confirmation of Hunter's and Pritchard's theory – there being a discrepancy of the order of  $0.1 \text{ cm}^{-1}$  between the predicted and experimental frequencies. However, Hunter and Pritchard never presented a proof of the convergence of their numerical procedure, nor did they show the orthogonality of their basis functions. More accurate experiments by Spezeski (1977) and by Carrington *et al* (1982) showed the need for further theoretical improvement. This was also done by Wolneiwicz and Poll (1978) who performed a second order perturbation for the 'non-adiabatic' Hamiltonian in the space of 'adiabatic' wave functions calculated by Bishop (1974) using a 'clamped nuclei' approximation. Bishop and Cheung (1977) had also estimated the radiative corrections, to the vibrational–rotational energy levels of the  $\text{HD}^+$  molecule using an empirical formula. When these radiative corrections are added to the perturbative results of Wolneiwicz and Poll (1978), the agreement with the experiments is truly phenomenal – of the order of  $0.001 \text{ cm}^{-1}$  for the low lying levels and about  $0.01 \text{ cm}^{-1}$  for high values of  $\nu$  and  $J$ . Later on in the paper, we shall present a comparison of our results with those of Wolneiwicz and Poll (1978).

We wish to end this section with a final remark about the present work. In our earlier paper (Bhattacharjee *et al* 1983) we had calculated the energy eigenvalues of the three-body quantum mechanical problem (e.g. the  $\text{HD}^+$  molecule in the limit of infinitely heavy nuclei) as the *limits* of the successive truncations of *convergent* infinite Hill determinants. The energy eigenvalues and the eigenfunctions thus found were accurate to 1 part in  $10^8$  and the eigenfunctions were demonstrated to be orthogonal. With *these* eigenfunctions (called static eigenfunctions) as bases we have calculated the vibrational–rotational energy levels for the  $\text{HD}^+$  molecule in the  $1s\sigma_g$  electronic state in the BO and the adiabatic approximations.

The paper is arranged as follows. In §2 we review the theoretical formulation of the three-body problem in the 'adiabatic' and the 'non-adiabatic' approximations. In §3 we describe the evaluation of the nuclear potential (due to electronic motion) in the BO and the 'adiabatic' approximations. Section 4 deals with an accurate variational solution to the problem of nuclear motion. A comparative study of our results with those from experiments and the earlier theoretical papers (Hunter and Pritchard 1967; Wolneiwicz and Poll 1978) is presented in §5.

## 2. Theoretical formulation of the three-body problem

The non-relativistic Schrödinger equation for the three-body quantum mechanical problem with Coulomb interactions is:

$$\left\{ \frac{-\hbar^2}{2} \sum_{i=1}^3 \frac{1}{m_i} \nabla_i^2 + \sum_{i=1}^3 \sum_{j>i} \frac{Z_i Z_j}{|\mathbf{R}_j - \mathbf{R}_i|} \right\} \psi = E\psi, \quad (1)$$

where  $\mathbf{R}_1$ ,  $\mathbf{R}_2$ ,  $\mathbf{R}_3$  are the position vectors of the masses  $m_1$ ,  $m_2$  and  $m_3$ , respectively, and  $Z_i$  is the charge on the  $i$ th particle. Under the standard centre of mass and relative coordinate transformation, one gets:

$$-(\hbar^2/2M)\nabla_{\text{c.m.}}^2 \psi_{\text{c.m.}} = (E - E_I)\psi_{\text{c.m.}} \quad (2)$$

and

$$\begin{aligned} & \{ -(\hbar^2/2\mu_1)\nabla_a^2 - (\hbar^2/2\mu_2)\nabla_b^2 + V(|\mathbf{R}_a|, |\mathbf{R}_b|) \} \psi_I(\mathbf{R}_a, \mathbf{R}_b) \\ & = E_I \psi_I(\mathbf{R}_a, \mathbf{R}_b). \end{aligned} \quad (3)$$

Here  $\mathbf{R}_{c.m.}$  is the centre of mass (c.m.) of the three-body system,  $M = m_1 + m_2 + m_3$ ,  $(E - E_I)$  the kinetic energy of the centre of mass,  $\mathbf{R}_a = \mathbf{R}_1 - \mathbf{R}_2$ ,  $\mathbf{R}_b$  is the relative coordinate of  $m_3$  with respect to the c.m. of  $m_1$  and  $m_2$  [i.e.  $\mathbf{R}_3 - (m_1\mathbf{R}_1 + m_2\mathbf{R}_2)/(m_1 + m_2)$ ],  $E_I$  is the energy of internal motion and

$$\begin{aligned} \mu_1 &= m_1 m_2 / (m_1 + m_2), \\ \mu_2 &= m_3 (m_1 + m_2) / M. \end{aligned} \quad (4)$$

We now choose  $m_3 = m_e$  (the mass of an electron) and work in natural atomic units  $\hbar = m_e = e = 1$ . We further make use of the dimensional homogeneity of (3) and perform the transformations:

$$\begin{aligned} m_1 &= \alpha_1 m_3; \quad m_2 = \beta_1 m_3; \quad \gamma = 1 + [1/(\alpha_1 + \beta_1)]; \\ \mu_1' &= \alpha_1 \beta_1 \gamma / (\alpha_1 + \beta_1); \\ \epsilon_I &= E_I \gamma; \quad \mathbf{R}_{a'} = \gamma \mathbf{R}_a; \quad \mathbf{R}_{b'} = \gamma \mathbf{R}_b. \end{aligned} \quad (5)$$

Equation (3) can now be recast in the form

$$[-(1/2\mu_1')\nabla_{a'}^2 + H_0]\psi_I(\mathbf{R}_{a'}, \mathbf{R}_{b'}) = \epsilon_I \psi_I(\mathbf{R}_{a'}, \mathbf{R}_{b'}), \quad (6)$$

where

$$H_0 = -1/2\nabla_{b'}^2 - \frac{Z_1}{|\mathbf{R}_{b'} + [\alpha_1/(\alpha_1 + \beta_1)]\mathbf{R}_{a'}|} - \frac{Z_2}{|\mathbf{R}_{b'} - [\beta_1/(\alpha_1 + \beta_1)]\mathbf{R}_{a'}|} + \frac{Z_1 Z_2}{|\mathbf{R}_{a'}|} \quad (7)$$

The most general solution for the wave-function  $\psi_I(\mathbf{R}_{a'}, \mathbf{R}_{b'})$  is of the form (Born and Huang 1954)

$$\psi_I(\mathbf{R}_{a'}, \mathbf{R}_{b'}) = \sum_n \psi_n(\mathbf{R}_{a'}) \phi_n(\mathbf{R}_{a'}, \mathbf{R}_{b'}), \quad (8)$$

where  $\phi_n(\mathbf{R}_{a'}, \mathbf{R}_{b'})$  is the complete set of orthonormal wave functions for the electronic problem in the field of 'infinitely heavy' nuclei. These are solutions of

$$H_0 \phi_n(\mathbf{R}_{a'}, \mathbf{R}_{b'}) = \Phi_n(|\mathbf{R}_{a'}|) \phi_n(\mathbf{R}_{a'}, \mathbf{R}_{b'}). \quad (9)$$

In (9) the relative nuclear coordinate  $\mathbf{R}_{a'}$  plays only a parametric role, not a dynamic one. Using the orthogonality of the  $\phi_n$ , one can rewrite (6) in the form

$$\begin{aligned} & [-(1/2\mu_1')\nabla_{a'}^2 + \Phi_n(|\mathbf{R}_{a'}|) - \epsilon_I] \psi_n(\mathbf{R}_{a'}) \\ & + \sum_{n'} C_{nn'}(\mathbf{R}_{a'}, \nabla_{a'}) \psi_{n'}(\mathbf{R}_{a'}) = 0, \end{aligned} \quad (10)$$

where

$$C_{nn'} = A_{nn'} \nabla_{a'} + B_{nn'}, \quad (11)$$

$$A_{nn'} = -(1/\mu_1') \int \phi_n(\mathbf{R}_{a'}, \mathbf{R}_{b'}) \nabla_{a'} \phi_{n'}(\mathbf{R}_{a'}, \mathbf{R}_{b'}) d^3 \mathbf{R}_{b'} \quad (12)$$

and

$$B_{nn'} = (1/2\mu_1') \int \nabla_{a'} \phi_n(\mathbf{R}_{a'}, \mathbf{R}_{b'}) \cdot \nabla_{a'} \phi_{n'}(\mathbf{R}_{a'}, \mathbf{R}_{b'}) d^3 \mathbf{R}_{b'}. \quad (13)$$

It is trivial to show that  $A_{nn}$  is zero. Thus, (10) can be rewritten as:

$$\begin{aligned} &[-(1/2\mu'_1)\nabla_{a'}^2 + U_n(|\mathbf{R}_{a'}|) - \epsilon_I]\psi_n(\mathbf{R}_{a'}) \\ &+ \sum_{n' \neq n} C_{nn'}(\mathbf{R}_{a'}, \nabla_{a'})\psi_{n'}(\mathbf{R}_{a'}) = 0 \end{aligned} \quad (14)$$

with

$$U_n(|\mathbf{R}_{a'}|) = \Phi_n(|\mathbf{R}_{a'}|) + B_{nn}. \quad (15)$$

$\Phi_n$  represents the nuclear potential in the BO approximation, while  $U_n$  is the potential in the adiabatic approximation. The complete potential in the non-adiabatic approximation is the nonlocal form involving the term  $C_{nn'}$ . In the present work, we have attempted to solve (14) neglecting the non-adiabatic terms using the complete set of eigenfunctions  $\phi_n(\mathbf{R}_{a'}, \mathbf{R}_{b'})$  and eigenvalues  $\Phi_n(|\mathbf{R}_{a'}|)$  of the 'static' electronic problem found in Bhattacharjee *et al* (1983).

### 3. Numerical evaluation of the nuclear potential in the adiabatic approximation

In the adiabatic approximation, the nuclear motion, although coupled to the electronic motion, does not induce transitions among the electronic states [see (13) and (15)]. For the electronic ground state  $1s\sigma_g$  (denoted by  $n = 0$ ) the relevant part of the nuclear potential is

$$B_{00} = (1/2\mu'_1) \iint \{|\nabla_{a'}\phi_0(\mathbf{R}_{a'}, \mathbf{R}_{b'})\}^2 d^3\mathbf{R}_{b'}, \quad (16)$$

where the coordinate system has its origin at the centre of mass of the nuclei,  $\mathbf{R}_{a'}$  the relative distance between  $m_1$  and  $m_2$  and  $\mathbf{R}_{b'}$  the position of the electron. Since the 'static' electronic wave function is normalized at each  $|\mathbf{R}_{a'}| = R$ , one can write in the standard confocal ellipsoidal coordinates

$$\xi = (r_1 + r_2)R, \quad \eta = (r_1 - r_2)R, \quad \omega \quad (17)$$

$$\phi_0(\mathbf{R}_{a'}, \mathbf{R}_{b'}) = N_0(R)\chi_0(R, \xi, \eta, \omega). \quad (18)$$

As shown by us (Bhattacharjee *et al* 1983)

$$\begin{aligned} \chi_0(R, \xi, \eta, \omega) = & \left\{ \exp(-p\xi) (\xi+1)^\sigma \sum_{k=0}^{\infty} C_k [(\xi-1)/(\xi+1)]^k \right\} \\ & \times \sum_{l=1}^{\infty} a_l P_{2l-2}(\eta), \end{aligned} \quad (19)$$

where

$$p^2 = -1/2R^2[\Phi_0(R) - Z_1Z_2/R], \quad (20)$$

and

$$\sigma = (R/p) - 1. \quad (21)$$

The integral in (16) can now be expressed as a double summation over certain Whittaker functions (Gradshteyn and Ryzhik 1965). The details are tedious but

straightforward. Thus one gets

$$B_{0,0} = \frac{1}{2\mu'_1} \left\{ \frac{\pi}{4} N_0^2 R \left( \sum_{i=1}^6 t_i + \sum_{i=1}^2 z_i \right) + \frac{\pi}{2} N_0 \frac{\partial N_0}{\partial R} R^2 \sum_{i=1}^4 c_i \right. \\ \left. + \sum_{i=1}^{25} g_i + \sum_{i=1}^6 y_i + \left( \frac{\partial N_0}{\partial R} \right)^2 \frac{1}{N_0^2} \right\}. \quad (22)$$

Here each of the expressions  $t_i$ ,  $z_i$ ,  $c_i$ ,  $g_i$  and  $y_i$  is a double summation over some Whittaker functions of the type

$$\sum_{k,k'} f(k, k') C_k C_{k'} \Gamma(\lambda) W_{\lambda,\mu}(Z), \quad (23)$$

the indices  $\lambda$  and  $\mu$  depend on  $k$ ,  $k'$  and  $Z = 4p$  (Bateman Manuscript Project 1953) (for details see appendix A). To evaluate these double summations numerically one must have some idea of the convergence of the double sum over the indices  $k$  and  $k'$ . Using the Stirling formula for the asymptotic behaviour of  $\Gamma$ -functions and the asymptotic behaviour of the Whittaker functions (Gradshteyn and Ryzhik 1965),  $\lambda \sim c - k - k'$ , one gets

$$\Gamma(\lambda) W_{-\lambda,\mu}(Z) \underset{\lambda \rightarrow \infty}{\sim} (Z/4\lambda)^{1/4} \exp[-2(2\lambda Z)^{1/2}]. \quad (24)$$

Furthermore, as proved by us (Bhattacharjee *et al* 1983)

$$(C_{k+1}/C_k) \underset{k \rightarrow \infty}{\longrightarrow} 1 - 2(p/k)^{1/2} + O(1/k^2). \quad (25)$$

Thus all the double sums of the type (23) will be uniformly convergent. Retaining about fifteen terms each in the double sums yields results correct to at least eight significant places. Also as shown earlier (Bhattacharjee *et al* 1983)

$$(a_{l+2}/a_l) \underset{l \rightarrow \infty}{\longrightarrow} O(1/l^2). \quad (26)$$

The resultant integrals, (A49)–(A62), are also uniformly convergent sums and hence, to achieve eight figure accuracy, one needs only to keep about ten terms in each sum.

Clearly for an accurate evaluation of double summations of the type (25), one needs to compute Whittaker functions rather well. To the best of our knowledge, no reliable account of an accurate evaluation of the Whittaker functions, in regions of parameters that may be doubly asymptotic ( $\lambda$  and  $Z$  both large) has ever been published, much less used in a physical computation. Our method for numerical evaluation of  $W_{\lambda\mu}(z)$  for  $\lambda \approx 35$ ,  $\mu \sim 1$ ,  $Z \approx 20$ , correct to one part in  $10^8$  is outlined in appendix B.

The logarithmic integrals quoted in appendix A (A45–A48) can be expressed in terms of the derivatives of the Whittaker functions with respect to the indices  $\lambda$  or  $\mu$ . No well-known series expansion is found in the literature for such functions. Hence, we decided to evaluate these integrals using a 25-point Gauss–Laguerre quadrature, thereby yielding at least 8-figure accuracy. The derivatives  $\partial C_k/\partial R$ ,  $\partial a_l/\partial R$ ,  $\partial N_0/\partial R$ ,  $\partial \sigma/\partial R$  and  $\partial p/\partial R$  have also to be evaluated numerically. It is well known that a straightforward polynomial fit to numerical data for plotting the slope of the function always leads to truncations. Thus, we obtain a continued fraction fit of the function through the method of inverted differences. The differentiation of

this fitted continued fraction yields numerical derivatives accurate to about one part in  $10^8$ .

Thus all the expressions  $t_i$ ,  $z_i$ ,  $c_i$ ,  $g_i$  and  $y_i$  of appendix A can now be evaluated. Since we had already evaluated the 'static' energy eigenvalues (Bhattacharjee *et al* 1983) correct to 1 part in  $10^8$ , the overall accuracy of our nuclear potential computation in either the BO or the adiabatic approximation is 1 part in  $10^8$ .

#### 4. Solution of the nuclear wave equation

The nuclear wave function  $\psi'_0(R)$  satisfies the wave equation (14)

$$[-(1/2\mu'_1)\nabla_a^2 + U_0(R) - \epsilon_I]\psi'_0(R) = 0, \quad (27)$$

where  $\epsilon_I$  denotes the vibrational rotational  $(v, J)$  energy level of the nuclei,

$$U_0(R) = \Phi_0(R), \quad (28)$$

in the Born–Oppenheimer (BO) approximation, and

$$U_0(R) = \Phi_0(R) + B_{0,0}, \quad (29)$$

in the adiabatic approximation. Since the potential in either case is spherically symmetric, one can reduce the wave equation by the substitution:

$$\psi'_0(R) = R^J g_{v,J}(R) Y_{J,M}(\theta, \phi). \quad (30)$$

Finally one gets

$$\left\{ \frac{d^2}{dR^2} + \frac{2(J+1)}{R} \frac{d}{dR} + 2\mu'_1(\epsilon_I - U_0(R)) \right\} g_{v,J}(R) = 0. \quad (31)$$

To solve (31), one uses a variational principle. A plot of the potential clearly shows a harmonic-oscillator-like structure. Thus the low lying  $(v, J)$  levels are expected to be centred around a certain equilibrium distance  $R_E$  of the nuclei. A variational expansion of the type

$$g_{v,J}(R) = \exp(-1/2y^2) \sum_{m=0}^{\infty} A_m \Theta_m(y), \quad (32)$$

where

$$\Theta_m(y) = (2^m m! \pi^{1/2})^{-1/2} H_m(y), \quad (33)$$

$H_m(y)$  being the Hermite polynomial,

$$y = \alpha(R - R_E), \quad \alpha = (\mu'_1 k)^{1/4}. \quad (34)$$

$R_E$  is the equilibrium distance and  $k$  is the stiffness constant, which should be particularly suitable for our problem. On substituting the ansatz (32) in (31), the wave equation reduces to the secular form

$$|\mathcal{H} - \epsilon_I S| = 0, \quad (35)$$

where

$$\mathcal{H}_{mn} = \int_{-\alpha R_E}^{\infty} \exp(-y^2/2) \Theta_m(y) \left( -\frac{d^2}{dR^2} - \frac{2(J+1)}{R} \frac{d}{dR} + U_0(R) \right) \times \exp(-y^2/2) \Theta_n(y) dy, \quad (36)$$

$$\mathcal{S}_{mn} = \int_{-\alpha R_E}^{\infty} \exp(-y^2) \Theta_m(y) \Theta_n(y) dy. \quad (37)$$

These integrals are evaluated using a combination of Simpson's rule and Newton's 3/8 rule. The secular equation (35) is then solved for the energy eigenvalues using the standard IBM Scientific Subroutine package. The eigenvalues are computed using  $5 \times 5$ ,  $10 \times 10$ ,  $15 \times 15$  and  $20 \times 20$  matrices. We show in tables 1 and 2 the convergence of various  $v, J$  energy levels of the  $HD^+$  molecule in the BO and the adiabatic approximations, respectively.

## 5. Results and discussion

We first report our results on the vibrational-rotational energy levels of the  $H_2^+$  molecule in the BO approximation along with those obtained by Hunter and Pritchard (1967). These are shown in table 3. It should be noted that the energy levels reported by us are consistently lower than the ones obtained by Hunter and Pritchard (1967). Since we have used a variational procedure for estimating the energy levels, and as discussed earlier, our numerical procedure seems to be free

**Table 1.** Convergence (showing the numerical stability) of the vibrational-rotational ( $v, J$ ) energy levels for the  $HD^+$  in the Born-Oppenheimer approximation.

$(v, J)$	Energy calculated with $15 \times 15$ matrices in units of $\mu_2^{-1} = 1$	Energy calculated with $20 \times 20$ matrices in units of $\mu_2^{-1} = 1$
(0,0)	-0.5980912143904	-0.5980912143960
(1,0)	-0.5893729503489	-0.589372950673
(2,0)	-0.5810928920305	-0.58109294572
(3,0)	-0.573235772321	-0.573238115462
(0,1)	-0.5978913193175	-0.5978913193197
(1,1)	-0.58918218315837	-0.5891821834022
(2,1)	-0.5809110018880	-0.580911029035
(3,1)	-0.573063326248	-0.573064826452
(0,2)	-0.5974927256149	-0.5974927256152
(1,2)	-0.5888018015923	-0.5888018018166
(2,2)	-0.5805482918897	-0.5805483070056
(3,2)	-0.5727182880570	-0.5727192900602
(0,3)	-0.5968978028556	-0.59689780285678
(1,3)	-0.5882340890285	-0.5882340891886
(2,3)	-0.58000697050486	-0.5800069810595
(3,3)	-0.5722029548319	-0.5722036359485

**Table 2.** Convergence (showing the numerical stability) of the vibrational-rotational ( $\nu, J$ ) energy levels for the  $\text{HD}^+$  in the adiabatic approximation.

$(\nu, J)$	Energy calculated with $15 \times 15$ matrices in units of $\mu_2^{-1} = 1$	Energy calculated with $20 \times 20$ matrices in units of $\mu_2^{-1} = 1$
(0,0)	-0.5980306649362	-0.5980306649417
(1,0)	-0.5893134758705	-0.5893134761971
(2,0)	-0.5810344169400	-0.5810344708600
(3,0)	-0.5731782142855	-0.5731805658438
(0,1)	-0.5978307994191	-0.59783079942136
(1,1)	-0.5891227365139	-0.58912273675883
(2,1)	-0.5808525530387	-0.5808525803175
(3,1)	-0.5730057958317	-0.5730073015029
(0,2)	-0.5974322645952	-0.5974322645955
(1,2)	-0.5887424103911	-0.5887424106154
(2,2)	-0.5804898951693	-0.5804899103624
(3,2)	-0.5726608081420	-0.5726618138116
(0,3)	-0.5968364295767	-0.5968364295779
(1,3)	-0.5881747804351	-0.5881747805957
(2,3)	-0.5799486513899	-0.5799486619943
(3,3)	-0.5721455485833	-0.5721462323434

**Table 3.** Comparison between our calculated values and those calculated by Hunter and Pritchard (1967) for the vibrational-rotational ( $\nu, J$ ) energy levels of the  $\text{H}_2^+$  in the BO approximation.

$(\nu, J)$	BO energy for $\text{H}_2^+$ as calculated by Hunter and Pritchard (1967) in atomic units	BO energy for $\text{H}_2^+$ as calculated by us in atomic units
(0,0)	-0.5972283	-0.59728814
(0,1)	-0.5872474	-0.5873036

**Table 4.** The vibrational-rotational ( $\nu, J$ ) energy levels, calculated by us, for the  $\text{HD}^+$  in the BO and adiabatic approximation.

	$\nu = 0$	$\nu = 1$	$\nu = 2$	$\nu = 3$
<i>BO energies in units of <math>\mu_2^{-1} = 1</math></i>				
$J = 0$	-0.59809121439	-0.5893729506	-0.58109294	-0.57323811
$J = 1$	-0.597891319319	-0.5891821834	-0.58091102	-0.57306482
$J = 2$	-0.597492725615	-0.5888018018	-0.580548307	-0.5727192
$J = 3$	-0.59689780285	-0.5882340891	-0.580006981	-0.5722036
<i>Adiabatic energies in units of <math>\mu_2^{-1} = 1</math></i>				
$J = 0$	-0.5980306649	-0.589313476	-0.58103447	-0.5731805
$J = 1$	-0.59783079942	-0.5891227367	-0.58085258	-0.5730073
$J = 2$	-0.597432264595	-0.5887424106	-0.58048991	-0.57266181
$J = 3$	-0.596837429577	-0.5881747805	-0.57994866	-0.5721462



**Table 5.** Comparison in values of the transition frequencies of the vibrational-rotational ( $v, J$ ) energy levels as observed in experiments, values calculated by us and the values reported by other authors.

Transition levels ( $v, J$ )-( $v', J'$ )	Experimental values for the transition frequencies ( $cm^{-1}$ )	Transition frequencies as calculated by us in the BO approximation ( $cm^{-1}$ )	Transition frequencies as calculated by HP* in adiabatic approximation ( $cm^{-1}$ )	Transition frequencies as calculated by us in the adiabatic approximation ( $cm^{-1}$ )	Transition frequencies in the non-adiabatic approximation by HP* ( $cm^{-1}$ )	Non-adiabatic values** ( $cm^{-1}$ )
(1,0)-(0,1)	1869-134	1869-226	1869-28	1868-997	1869-21	1869-135
(1,1)-(0,2)	1823-533	1823-621	1823-67	1823-399	1823-59	1823-533
(1,2)-(0,3)	1776-459	1776-544	—	1776-328	—	1776-461
(2,1)-(1,0)	1856-778	1856-841	1856-92	1856-615	1856-82	1856-779
(3,1)-(2,0)	1761-616	1761-649	1761-74	1761-440	1761-48	1761-616
(3,2)-(2,1)	1797-522	1797-570	1797-64	1797-340	1797-41	1797-519
(3,1)-(2,2)	1642-108	1642-137	1642-23	1641-945	1641-98	1642-111
(3,3)-(2,2)	1831-083	1831-21	—	1830-900	—	1831-078

\* HP - Hunter and Pritchard (1967); \*\* Wolniewicz and Poll (1978).

from errors to the extent of at least one part in  $10^8$ , we believe our results to provide better lower bounds to the actual energy levels.

Our results in the BO as well as the adiabatic approximation are reported in table 4. From these results it is easy to provide a comprehensive comparison of our results with those of other authors as well as with the experiments. For the sake of convenience, we have displayed in table 5 the transition frequencies for the  $\text{HD}^+$  molecule as computed by us in the BO and the adiabatic approximations, the ones calculated by Hunter and Pritchard (1967) in the adiabatic and nonadiabatic approximations, the nonadiabatic results of Wolneiwicz and Poll (1978) and the frequencies found in experiments (Carrington *et al* 1982).

It is to be noted that the transition frequencies obtained by us, in the BO approximation are almost the same as those reported by Hunter and Pritchard (1967) in their most accurate nonadiabatic computation; the difference between these frequencies seems to be of the order of  $0.01 \text{ cm}^{-1}$ – $0.1 \text{ cm}^{-1}$ . As we have already discussed the superiority of the BO procedure (see table 3), very little needs to be said in comparing our results with those of Hunter and Pritchard.

The next improvement occurs in our results of the adiabatic approximation. These frequencies are consistently lower than experiments by almost the same amount that the BO ones as reported by us are higher. Thus the situation vis-a-vis agreement with experiment in our calculations does not seem to have improved. However, there seems to be scope for improvement in our calculations. The nonadiabatic corrections and the relativistic effects like spin-spin and spin-orbit couplings, radiative corrections etc., may be taken into account.

It should be noted that the theoretical results of Wolneiwicz and Poll (1978) agree extremely well with experiments. It is of interest to observe that the general order of magnitude of nonadiabatic corrections in their paper is of the order of  $0.1 \text{ cm}^{-1}$  and the radiative corrections are of the order of  $0.008 \text{ cm}^{-1}$  for almost all frequencies. Further, the discrepancy between our adiabatic result and that from the experiments is of the order mentioned above. Work is in progress on the nonadiabatic and other effects.

We conclude this with a final remark about the extreme precision of the work of Wolneiwicz and Poll (1978). They used second order perturbation theory for their nonadiabatic calculations, in the space of the adiabatic wave functions computed by Bishop and Cheung (1974). It may be noted that Bishop and Cheung (1974) gave no proof regarding the orthonormality of these adiabatic wave functions. It is also claimed in their work that the evaluation of the infinite sum in the second order perturbation energy converges to a limit with an increasing number of terms, although no detailed numerical figures are given in support of the above assertion.

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**Appendix A**

$$t_1 = p^2 \left[ \alpha^2 H \sum_{k,k'} C_k C_{k'} \delta_{1,1}^{k,k'} + S1 \sum_{k,k'} C_k C_{k'} \delta_{1,0}^{k,k'} \right], \quad (A1)$$

$$t_2 = -2p\sigma \left[ \alpha^2 H \sum_{k,k'} C_k C_{k'} \delta_{2,1}^{k,k'} + S1 \sum_{k,k'} C_k C_{k'} \delta_{2,0}^{k,k'} \right], \quad (A2)$$

$$t_3 = -4p \left[ \alpha^2 H \sum_{k,k'} (k+1) C_{k+1} C_{k'} \delta_{3,1}^{k,k'} + S1 \sum_{k,k'} (k+1) C_{k+1} C_{k'} \delta_{3,0}^{k,k'} \right], \quad (A3)$$

$$t_4 = \sigma^2 \left[ \alpha^2 H \sum_{k,k'} C_k C_{k'} \delta_{3,1}^{k,k'} + S1 \sum_{k,k'} C_k C_{k'} \delta_{3,0}^{k,k'} \right], \quad (A4)$$

$$t_5 = 4\sigma \left[ \alpha^2 H \sum_{k,k'} (k+1) C_{k+1} C_{k'} \delta_{4,1}^{k,k'} + S1 \sum_{k,k'} (k+1) C_{k+1} C_{k'} \delta_{4,0}^{k,k'} \right], \quad (A5)$$

$$t_6 = 4 \left[ \alpha^2 H \sum_{k,k'} (k+1)(k'+1) C_{k+1} C_{k'+1} \delta_{5,1}^{k,k'} + S1 \sum_{k,k'} (k+1)(k'+1) C_{k+1} C_{k'+1} \delta_{5,0}^{k,k'} \right], \quad (A6)$$

$$z_1 = A \sum_{k,k'} C_k C_{k'} \delta_{1,1}^{k,k'}, \quad (A7)$$

$$z_2 = -\alpha^2 B \sum_{k,k'} C_k C_{k'} \delta_{1,0}^{k,k'}, \quad (A8)$$

$$c_1 = -pS1 \sum_{k,k'} C_k C_{k'} (\delta_{0,0}^{k,k'} - \delta_{1,0}^{k,k'}), \quad (A9)$$

$$c_2 = \sigma S1 \sum_{k,k'} C_k C_{k'} (\delta_{1,0}^{k,k'} - \delta_{2,0}^{k,k'}), \quad (A10)$$

$$c_3 = 2S1 \sum_{k,k'} (k+1) C_{k+1} C_{k'} (\delta_{2,0}^{k,k'} - \delta_{3,0}^{k,k'}), \quad (A11)$$

$$c_4 = F \sum_{k,k'} C_k C_{k'} \delta_{1,1}^{k,k'}, \quad (A12)$$

$$y_1 = -\frac{\pi}{2} N_0 \frac{\partial N_0}{\partial R} R^3 \frac{\partial p}{\partial R} \left\{ \sum_{k,k'} C_k C_{k'} [H(\delta_{2,2}^{k,k'} + \delta_{1,1}^{k,k'}) + S1(\delta_{0,0}^{k,k'} - \delta_{1,0}^{k,k'})] \right\}, \quad (A13)$$

$$y_2 = -\frac{\pi}{2} N_0 \frac{\partial N_0}{\partial R} R^2 \left\{ \sum_{k,k'} C_k C_{k'} \{ [H(\delta_{2,2}^{k,k'} + \delta_{1,1}^{k,k'}) + S1(\delta_{2,1}^{k,k'} + \delta_{1,0}^{k,k'})] (-p) + \sigma [H(\delta_{3,2}^{k,k'} + \delta_{2,1}^{k,k'}) + S1(\delta_{3,1}^{k,k'} + \delta_{2,0}^{k,k'})] \} + 2 \sum_{k,k'} (k+1) C_{k+1} C_{k'} [H(\delta_{4,2}^{k,k'} + \delta_{3,1}^{k,k'}) + S1(\delta_{4,1}^{k,k'} + \delta_{3,0}^{k,k'})] \right\} \quad (A14)$$

$$y_3 = -\frac{\pi}{2} N_0 \frac{\partial N_0}{\partial R} R^2 \left[ \sum_{k,k'} C_k C_{k'} (F \delta_{1,1}^{k,k'} - N1 \delta_{1,0}^{k,k'}) \right], \quad (A15)$$

$$y_4 = \frac{\pi}{2} \mathcal{N}_0 \frac{\partial \mathcal{N}_0}{\partial R} R^3 \left[ \sum_{k,k'} C_k C_{k'} (O1 \delta_{1,1}^{k,k'} + (O1 - P1)) \delta_{1,0}^{k,k'} \right], \tag{A16}$$

$$g_1 = \frac{\pi}{4} \mathcal{N}_0^2 R^3 \left( \frac{\partial p}{\partial R} \right)^2 \left\{ \sum_{k,k'} C_k C_{k'} [H(\delta_{1,2}^{k,k'} + \delta_{1,1}^{k,k'}) + S1(\delta_{1,1}^{k,k'} + \delta_{1,0}^{k,k'})] \right\}, \tag{A17}$$

$$g_2 = -\frac{\pi}{2} \mathcal{N}_0^2 R^2 \frac{\partial p}{\partial R} H \left\{ \sum_{k,k'} C_k C_{k'} [p(\delta_{1,2}^{k,k'} + \delta_{1,1}^{k,k'}) - \sigma(\delta_{2,2}^{k,k'} + \delta_{2,1}^{k,k'})] - 2 \sum_{k,k'} (k+1) C_{k+1} C_{k'} (\delta_{3,2}^{k,k'} + \delta_{3,1}^{k,k'}) \right\}, \tag{A18}$$

$$g_3 = -\frac{\pi}{2} \mathcal{N}_0^2 R^2 \frac{\partial p}{\partial R} N1 \sum_{k,k'} C_k C_{k'} (\delta_{0,0}^{k,k'} - \delta_{1,0}^{k,k'}), \tag{A19}$$

$$g_4 = -\frac{\pi}{2} \mathcal{N}_0^2 R^3 \frac{\partial p}{\partial R} \sum_{k,k'} C_k C_{k'} \{ O1 (\delta_{2,2}^{k,k'} + \delta_{1,1}^{k,k'}) + (O1 - P1) (\delta_{0,0}^{k,k'} - \delta_{1,0}^{k,k'}) \}, \tag{A20}$$

$$g_5 = \frac{\pi}{4} \mathcal{N}_0^2 R p^2 \sum_{k,k'} C_k C_{k'} \{ H \delta_{1,2}^{k,k'} + D \delta_{1,1}^{k,k'} - S1 \delta_{1,0}^{k,k'} \}, \tag{A21}$$

$$g_6 = -\pi \mathcal{N}_0^2 R p \sum_{k,k'} (k+1) C_{k+1} C_{k'} \{ H \delta_{3,2}^{k,k'} + D \delta_{3,1}^{k,k'} - S1 \delta_{3,0}^{k,k'} \}, \tag{A22}$$

$$g_7 = -\frac{\pi}{2} \mathcal{N}_0^2 R p \sigma \sum_{k,k'} C_k C_{k'} \{ H \delta_{2,2}^{k,k'} + D \delta_{2,1}^{k,k'} - S1 \delta_{2,0}^{k,k'} \}, \tag{A23}$$

$$g_8 = \frac{\pi}{4} \mathcal{N}_0^2 R \sigma^2 \sum_{k,k'} C_k C_{k'} \{ H \delta_{3,2}^{k,k'} + D \delta_{3,1}^{k,k'} - S1 \delta_{3,0}^{k,k'} \}, \tag{A24}$$

$$g_9 = \pi \mathcal{N}_0^2 R \sum_{k,k'} (k+1)(k'+1) C_{k+1} C_{k'+1} \{ H \delta_{5,2}^{k,k'} + D \delta_{5,1}^{k,k'} - S1 \delta_{5,0}^{k,k'} \}, \tag{A25}$$

$$g_{10} = \pi \mathcal{N}_0^2 R \sigma \sum_{k,k'} (k+1) C_{k+1} C_{k'} \{ H \delta_{4,2}^{k,k'} + D \delta_{4,1}^{k,k'} - S1 \delta_{4,0}^{k,k'} \}, \tag{A26}$$

$$g_{11} = \frac{\pi}{2} \mathcal{N}_0^2 R^2 O1 \left\{ \sum_{k,k'} C_k C_{k'} [p(\delta_{2,2}^{k,k'} + \delta_{1,1}^{k,k'}) - \sigma(\delta_{3,2}^{k,k'} + \delta_{2,1}^{k,k'})] - 2 \sum_{k,k'} (k+1) C_{k+1} C_{k'} (\delta_{4,2}^{k,k'} + \delta_{3,1}^{k,k'}) \right\}, \tag{A27}$$

$$g_{12} = -\frac{\pi}{4} \mathcal{N}_0^2 R \sum_{k,k'} C_k C_{k'} \{ (A + B) \delta_{1,1}^{k,k'} + M1 \delta_{1,0}^{k,k'} \}, \tag{A28}$$

$$g_{13} = \frac{\pi}{2} \mathcal{N}_0^2 R^2 N2 \sum_{k,k'} C_k C_{k'} \delta_{1,0}^{k,k'}, \tag{A29}$$

$$g_{14} = \frac{\pi}{4} \mathcal{N}_0^2 R^3 \sum_{k,k'} C_k C_{k'} \{ O2 \delta_{1,1}^{k,k'} + (O2 - P2) \delta_{1,0}^{k,k'} \}, \tag{A30}$$

$$g_{15} = \frac{\pi}{2} \mathcal{N}_0^2 R^3 \frac{\partial p}{\partial R} \frac{\partial \sigma}{\partial R} \sum_{k,k'} C_k C_{k'} \{ D \mathcal{C}_{1,1}^{k,k'} - H \mathcal{A}_{1,1}^{k,k'} \}, \tag{A31}$$

$$g_{16} = \frac{\pi}{4} N_0^2 R^3 \left( \frac{\partial \sigma}{\partial R} \right)^2 \sum_{k, k'} C_k C_{k'} \{ H \mathcal{F}_2^{k, k'} + S1 \mathcal{F}_1^{k, k'} \}, \quad (A32)$$

$$g_{17} = \frac{\pi}{2} N_0^2 R^2 \left( \frac{\partial \sigma}{\partial R} \right) H \left[ \sum_{k, k'} (p \mathcal{C}_{1,0}^{k, k'} - \sigma \mathcal{C}_{2,0}^{k, k'}) C_k C_{k'} - 2 \sum_{k, k'} \mathcal{C}_{3,0}^{k, k'} (k+1) C_{k+1} C_{k'} \right], \quad (A33)$$

$$g_{18} = \frac{\pi}{2} N_0^2 R^2 \frac{\partial \sigma}{\partial R} N1 \sum_{k, k'} C_k C_{k'} \mathcal{D}_0^{k, k'}, \quad (A34)$$

$$g_{19} = \frac{\pi}{2} N_0^2 R^3 \frac{\partial \sigma}{\partial R} \sum_{k, k'} C_k C_{k'} \{ O1 \mathcal{D}_1^{k, k'} + (O1 - P1) \mathcal{D}_0^{k, k'} \}, \quad (A35)$$

$$g_{20} = -\frac{\pi}{2} N_0^2 R^3 \frac{\partial p}{\partial R} \sum_{k, k'} C_k \frac{\partial C_{k'}}{\partial R} \{ H(\delta_{2,2}^{k, k'} + \delta_{1,1}^{k, k'}) + S1(\delta_{0,0}^{k, k'} - \delta_{1,0}^{k, k'}) \}, \quad (A36)$$

$$g_{21} = \frac{\pi}{2} N_0^2 R^3 \frac{\partial \sigma}{\partial R} \sum_{k, k'} C_k \frac{\partial C_{k'}}{\partial R} \{ H \mathcal{D}_1^{k, k'} + S1 \mathcal{D}_0^{k, k'} \}, \quad (A37)$$

$$g_{22} = \frac{\pi}{2} N_0^2 R^2 H \left\{ \sum_{k, k'} C_k \frac{\partial C_{k'}}{\partial R} [p(\delta_{2,2}^{k, k'} + \delta_{1,1}^{k, k'}) - \sigma(\delta_{3,2}^{k, k'} + \delta_{2,1}^{k, k'})] - 2 \sum_{k, k'} (k+1) C_{k+1} \frac{\partial C_{k'}}{\partial R} (\delta_{4,2}^{k, k'} + \delta_{3,1}^{k, k'}) \right\}, \quad (A38)$$

$$g_{23} = \frac{\pi}{2} N_0^2 R^2 N1 \sum_{k, k'} C_k \frac{\partial C_{k'}}{\partial R} \delta_{1,0}^{k, k'}, \quad (A39)$$

$$g_{24} = \frac{\pi}{4} N_0^2 R^3 \sum_{k, k'} \frac{\partial C_k}{\partial R} \frac{\partial C_{k'}}{\partial R} (H \delta_{1,1}^{k, k'} + S1 \delta_{1,0}^{k, k'}), \quad (A40)$$

$$g_{25} = \frac{\pi}{2} N_0^2 R^3 \sum_{k, k'} C_k \frac{\partial C_{k'}}{\partial R} [O1 \delta_{1,1}^{k, k'} + (O1 - P1) \delta_{1,0}^{k, k'}], \quad (A41)$$

$$y_5 = \frac{\pi}{2} N_0 \frac{\partial N_0}{\partial R} R^3 \sum_{k, k'} C_k \frac{\partial C_{k'}}{\partial R} (H \delta_{1,1}^{k, k'} + S1 \delta_{1,0}^{k, k'}), \quad (A42)$$

$$y_6 = \frac{\pi}{2} N_0 \frac{\partial N_0}{\partial R} R^3 \frac{\partial \sigma}{\partial R} \sum_{k, k'} C_k C_{k'} \{ H \mathcal{D}_1^{k, k'} + S1 \mathcal{D}_0^{k, k'} \}, \quad (A43)$$

$$\delta_{l,j}^{k,k'} = \frac{\Gamma(k_+ + j + 1)}{2p^{[\sigma + (3+2j-l)/2]}} W_{[\sigma - k_+ - (l-1)/2]}^{(4p)}(\sigma + j + 1 - l/2), \quad (A44)$$

$k_+$  being  $k + k'$ ,

$$\mathcal{C}_{l,j}^{k,k'} = \frac{\exp(-2p)}{2p^{(2\sigma + 5 - l - 2j)}} \int_0^\infty \exp(-y)(y + 4p)^{(2\sigma - k_+ - l - j + 2)} y^{(k_+ - j + 1)} (y + 2p) \times \ln(2 + y/2p) dy, \quad (A45)$$

$$\mathfrak{F}_l^{k,k'} = \frac{\exp(-2p)}{2p^{(2\sigma+2l-1)}} \int_0^\infty \exp(-y)(y+4p)^{(2\sigma-k_++l-1)} y^{(k_++l-1)} \times [\ln(2+y/2p)]^2 dy, \tag{A46}$$

$$\mathfrak{D}_l^{k,k'} = \frac{\exp(-2p)}{2p^{(2\sigma+2l+1)}} \int_0^\infty \exp(-y)(y+4p)^{(2\sigma-k_++l)} y^{(k_++l)} \ln(2+y/2p) dy, \tag{A47}$$

$$\mathfrak{A}_1^{k,k'} = \frac{\exp(-2p)}{2p^{(2\sigma+4)}} \int_0^\infty \exp(-y)(y+4p)^{(2\sigma-k_+)} y^{k_+} (y+2p)^3 \ln(2+y/2p) dy, \tag{A48}$$

$$H = 2 \sum_{l=1}^\infty a_l^2 \frac{1}{(4l-3)}, \tag{A49}$$

$$D = 4 \sum_{l=1}^\infty a_l a_{l+1} \frac{2l(2l-1)}{(4l-3)(4l-1)(4l+1)} + 2 \sum_{l=1}^\infty a_l^2 \frac{1}{(4l-3)^2} \left\{ \frac{(2l-1)^2}{(4l-1)} + \frac{(2l-2)^2}{(4l-5)} \right\}, \tag{A50}$$

$$A = 2 \sum_{l=2}^\infty \sum_{l'=2}^\infty (2a_l a_{l'} - \delta_{l,l'} a_l^2) \sum_{k=0}^{l'-2} (4l' - 4k - 5), \tag{A51}$$

$$B = 2 \sum_{l=2}^\infty a_l^2 \frac{(2l-1)^2}{(4l-3)}, \tag{A52}$$

$$F = 2 \left( \sum_{l=1}^\infty \sum_{l'=l+1}^\infty a_l a_{l'} + \sum_{l=2}^\infty a_l^2 \frac{(2l-2)}{(4l-3)} \right), \tag{A53}$$

$$M1 = 2 \sum_{l=2}^\infty a_l^2 \left\{ \frac{2l(2l-1)(2l-2)^2}{(4l-1)(4l-3)^2} + \frac{(2l-3)(2l-2)(2l-1)^2}{(4l-5)(4l-3)^2} \right\} + 4 \sum_{l=2}^\infty \frac{2l(2l+1)(2l-1)(2l-2)}{(4l+1)(4l-1)(4l-3)} a_l a_{l+1}, \tag{A54}$$

$$N1 = -2 \left[ \sum_{l=2}^\infty a_l^2 \frac{(2l-1)(2l-2)}{(4l-1)(4l-3)(4l-5)} + \sum_{l=1}^\infty a_l a_{l+1} \frac{2l(2l+1)(2l-1)}{(4l+1)(4l-1)(4l-3)} - \sum_{l=2}^\infty a_l a_{l+1} \frac{2l(2l-1)(2l-2)}{(4l+1)(4l-1)(4l-3)} \right], \tag{A55}$$

$$S1 = H - D, \tag{A56}$$

$$\begin{aligned}
 N2 = -2 \left[ \sum_{l=2}^{\infty} \frac{\partial a_l}{\partial R} a_{l+1} \frac{(2l+1)(2l-1)2l}{(4l+1)(4l-1)(4l-3)} \right. \\
 + \sum_{l=2}^{\infty} \frac{\partial a_l}{\partial R} a_l \frac{(2l-1)(2l-2)}{(4l-1)(4l-3)(4l-5)} \\
 \left. - \sum_{l=2}^{\infty} \frac{\partial a_{l+1}}{\partial R} a_l \frac{2l(2l-1)(2l-2)}{(4l+1)(4l-1)(4l-3)} \right], \tag{A57}
 \end{aligned}$$

$$O1 = 2 \sum_{l=2}^{\infty} a_l \frac{\partial a_l}{\partial R} \frac{1}{(4l-3)}, \tag{A58}$$

$$O2 = 2 \sum_{l=2}^{\infty} \left( \frac{\partial a_l}{\partial R} \right)^2 \frac{1}{(4l-3)}, \tag{A59}$$

$$\begin{aligned}
 P1 = 2 \left\{ \sum_{l=2}^{\infty} a_{l+1} \frac{\partial a_l}{\partial R} \frac{2l(2l-1)}{(4l+1)(4l-1)(4l-3)} \right. \\
 + \sum_{l=2}^{\infty} a_l \frac{\partial a_l}{\partial R} \frac{1}{(4l-3)^2} \left[ \frac{(2l-1)^2}{(4l-1)} + \frac{(2l-2)^2}{(4l-5)} \right] \\
 \left. + \sum_{l=1}^{\infty} a_l \frac{\partial a_{l+1}}{\partial R} \frac{2l(2l-1)}{(4l+1)(4l-1)(4l-3)} \right\}, \tag{A60}
 \end{aligned}$$

$$\begin{aligned}
 P2 = 4 \sum_{l=2}^{\infty} \frac{\partial a_{l+1}}{\partial R} \frac{\partial a_l}{\partial R} \frac{2l(2l-1)}{(4l+1)(4l-1)(4l-3)} \\
 + 2 \sum_{l=2}^{\infty} \left( \frac{\partial a_l}{\partial R} \right)^2 \frac{1}{(4l-3)^2} \left[ \frac{(2l-1)^2}{(4l-1)} + \frac{(2l-2)^2}{(4l-5)} \right]. \tag{A61}
 \end{aligned}$$

### Appendix B

To evaluate the Whittaker functions  $W_{a,b}(z)$  numerically, one recasts them as confluent hypergeometric functions (Bateman Manuscript Project 1953),

$$W_{a,b}(4p) = \exp(-2p)(4p)^{(2b+1)} \psi[(1/2-b+a), (2b+1), 4p], \tag{B1}$$

where

$$\begin{aligned}
 \psi(\alpha, \beta, z) = \frac{\Gamma(1-\beta)}{\Gamma(\alpha-\beta+1)} \phi(\alpha, \beta, z) \\
 + \frac{\Gamma(\beta-1)}{\Gamma(\alpha)} z^{(1-\beta)} \phi[(\alpha-\beta+1), (2-\beta), z], \tag{B2}
 \end{aligned}$$

and

$$\phi(\alpha, \beta, z) = \frac{\Gamma(\beta)}{\Gamma(\alpha)} \sum_{n=0}^{\infty} \frac{\Gamma(\alpha+n)}{\Gamma(\beta+n)} \frac{z^n}{\Gamma(n+1)}. \tag{B3}$$

For our purpose, we need integral values of  $\alpha$  and fractional values of  $\beta$ .

Further, as discussed in §3 we require  $\alpha \approx 35$ , for the  $1s\sigma_g$  state at various values of  $R'$  varies over a small range, while  $z$  varies almost from 0 to 20 or 25. A straightforward evaluation of the series expansion in (B2) suffers from the severe defect of numerical round-off errors in the region of moderate  $z$ , e.g.  $2.8 \leq z \leq 16.0$ . For the  $1s\sigma_g$  state for  $\beta = -1.652564622694$ ,  $z = 3.4097454608$  at  $\alpha = 1$ , the two series in (B2) cancel each other resulting in the loss of three significant digits, whereas at  $\alpha = 8$  the loss in accuracy is eight significant digits. For  $z = 2.8$  and  $\alpha$  (moderate) the loss in accuracy was insignificant. Thus for  $z \leq 2.8$  and higher values of  $\alpha$ , one could try to use a recurrence relation of the type (Bateman Manuscript Project 1953)

$$\psi(\alpha+) = \frac{1}{[\alpha(\alpha-\beta+1)]} [(2\alpha-\beta+z)\psi(\alpha) - \psi(\alpha-)], \quad (\text{B4})$$

where  $\alpha \pm = \alpha \pm 1$ . Unfortunately (B4) is subject to serious numerical truncations and the method outlined above has to be abandoned.

In the region of large numerical truncations (i.e.  $z \geq 2.6$  and  $\alpha$  moderate to large) an integral representation,

$$\psi(\alpha, \beta, z) = \frac{1}{\Gamma(\alpha)z^{(\alpha-1)}} \int_0^\infty \exp(-t)t^{(\alpha-1)}(t+z)^{(\beta-\alpha-1)} dt, \quad (\text{B5})$$

is found useful. A straightforward numerical evaluation of the integral in (B5) using 24-point and 32-point Gauss-Laguerre quadrature for various values of  $\alpha$  and  $\beta$  and  $1 \leq z \leq 16$  was found to be convergent to about eight to ten significant places. For  $z < 1$ , the singularity in the factor  $(t+z)^{\beta-\alpha-1}$  in (B5) starts coming closer and closer to the lower limit of integration and thus renders the numerical procedure unreliable. However, even for  $z < 1$  for large  $\alpha \sim 25$  the Gauss-Laguerre quadrature will work quite well, because a large number of derivatives of the integrand at the lower limit would be zero, thus rendering the integrand smooth near  $t = 0$ . Thus the strategy for the evaluation of the Whittaker functions becomes clear. For large values of  $\alpha$  and  $z$ , given  $\beta$  and  $z$ , one uses (B5) to evaluate the Whittaker function. For the same  $\beta$  and  $z$  and lower values of  $\alpha$  the  $W_{a,b}$ 's are evaluated by the backward recurrence relation

$$\psi(\alpha-) = (2\alpha-\beta+z)\psi(\alpha) - \alpha(\alpha-\beta+1)\psi(\alpha+). \quad (\text{B6})$$

For large  $\alpha$ , the multiplying factors of the various in  $\psi$ 's (B6) are of order  $2\alpha$  and  $-\alpha^2$  and for small  $\alpha$  they are  $z-\beta$  and  $\alpha(\beta-1)$ . In either case the multiplying factors are of different orders of magnitude and cannot lead to round-off errors. For different values of  $\beta$  one uses the recurrence relation,

$$\psi(\beta+) = (1/z)[(\beta-1+z)\psi+(\alpha+1-\beta)\psi(\beta-)], \quad (\text{B7})$$

where  $\beta \pm = \beta \pm 1$ . This relation for  $z \geq 4$  exhibits no truncations and was used in conjunction with (B6) and (B5) to evaluate all the Whittaker functions we needed, to at least an accuracy of one part in  $10^{+8}$ .



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