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## Perturbation Calculation of the Energy of the First Excited State $(2p\sigma)$ of $H_2^+$

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The electronic energy of the  $2\rho\sigma$  state of  $H_2^+$  is calculated by perturbation theory to third order using the Guillemin–Zener wavefunction as a zeroth-order function. The results agree quite well with the exact calculations except for small internuclear distances, as expected.

**R**ECENTLY,<sup>1</sup> a perturbation calculation to third order in energy has been carried out on the ground state of  $H_2^+$  starting with a simple zeroth-order function. In this note, we present a similar calculation on the  $2p\sigma$  state of  $H_2^+$ . In this calculation, the firstorder perturbation equation is solved, and the energy calculated to third-order.

The normalized zeroth-order wavefunction for the  $2p\sigma$  state is taken to be the Heitler-London function,

$$\psi^{(0)} = N \exp\left(-\frac{1}{2}Ra\lambda\right) \sinh\left(\frac{1}{2}(Rb\mu)\right). \tag{1}$$

The parameters a and b are functions of R, as is the normalization constant N, and  $\lambda$  and  $\mu$  are the usual spheroidal coordinates. At  $R = \infty$ ,  $\psi^{(0)}$  becomes the separated hydrogen atom and proton. But as  $R \rightarrow 0$ , from the definitions of  $\lambda$  and  $\mu$  (with the origin of the spherical coordinates taken at the midpoint of the line joining the two nuclei),

$$R\lambda \equiv (r^{2} + rR\cos\theta + \frac{1}{4}R^{2})^{1/2} + (r^{2} - rR\cos\theta + \frac{1}{4}R^{2})^{1/2},$$
  

$$R\lambda \rightarrow 2r + O(R^{2}),$$
  

$$R\mu \equiv (r^{2} + rR\cos\theta + \frac{1}{4}R^{2})^{1/2} - (r^{2} - rR\cos\theta + \frac{1}{4}R^{2})^{1/2},$$

 $R\mu \rightarrow R \cos\theta + O(R^3)$ .

Hence, we have upon expansion of  $\sinh \frac{1}{2}(Rb\mu)$ , and keeping terms of order R only,

$$\psi^{(0)} \rightarrow RbN(R \rightarrow 0) \exp(-ar) \cos\theta.$$

But,<sup>(2)</sup>  $N(R \rightarrow 0) \sim R^{-1}$ ; hence

$$\psi^{(0)}(R=0) \sim \exp(-ar) \cos\theta. \tag{2}$$

This wavefunction is *not* the correct limiting form for R=0, since the 2p state for the H atom has a node at r=0. Because of this, it is seen that the perturbation series begins to diverge for sufficiently small R.

The zeroth-order Hamiltonian corresponding to  $\psi^{(0)}$  is

$$\mathfrak{K}^{(0)} = T - (T\psi^{(0)}/\psi^{(0)}) + E^{(0)}, \qquad (3)$$

or

$$3C^{(0)} = -\frac{1}{2}\Delta - (2a/R) \left[ \lambda/(\lambda^2 - \mu^2) \right] -\frac{1}{2} (a^2 - b^2) \left[ (1 - \mu^2) / (\lambda^2 - \mu^2) \right] - \left[ 2b\mu/R(\lambda^2 - \mu^2) \right] \coth^{\frac{1}{2}}(Rb\mu) \quad (4)$$
  
and

$$E^{(0)} = -\frac{1}{2}a^2. \tag{5}$$

Kim and Chang<sup>2</sup> have used a wavefunction of the type of (1) and have minimized the expectation value of 3C with respect to a and b. We start with their wavefunction as  $\psi^{(0)}$ . The values of a and b are given in Ref. 2. Equation (4) should be compared with the  $3C^{(0)}$  corresponding to the ground-state wavefunction.<sup>1</sup> (They are not the same, of course).

The perturbation, V, is given by  $\mathfrak{K} - \mathfrak{K}^{(0)}$  or

$$V = \frac{-4\lambda}{R(\lambda^{2} - \mu^{2})} + \frac{2a\lambda}{R(\lambda^{2} - \mu^{2})} + \frac{1}{2}(a^{2} - b^{2})\left(\frac{1 - \mu^{2}}{\lambda^{2} - \mu^{2}}\right) + \frac{2b\mu}{R(\lambda^{2} - \mu^{2})} \coth^{\frac{1}{2}}(Rb\mu).$$
(6)

Thus, we must solve the first-order perturbation equation for (1):

$$(\mathcal{F}^{(0)} - E^{(0)})\psi^{(1)} + (V - E^{(1)})\psi^{(0)} = 0$$
(7)

in which

$$E^{(1)} \!= \! \left<\!\!\! \left<\!\!\! \psi^{(0)} \mid V \mid \psi^{(0)} \right>\!\! \left<\!\!\! \left<\!\!\! \psi^{(0)} \mid \psi^{(0)} \right>\!\!\! \right>$$

The procedure used to find  $\psi^{(1)}$  is to make the substitution:

$$\psi^{(1)} = [F_1(\lambda) + F_2(\mu)] \psi^{(0)}, \qquad (8)$$

where  $F_1$  and  $F_2$  depend only on the variable indicated. When (8) is substituted into (7), we find that (7) is

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<sup>&</sup>lt;sup>1</sup>R. Matcha, W. Lyon, and J. O. Hirschfelder, Theoretical Chemistry Institute (University of Wisconsin) Rept. No. 57, July 1964; W. Lyon, R. Matcha, W. A. Sanders, W. Meath, and J. O. Hirschfelder, J. Chem. Phys. 43, 1095 (1965).

<sup>&</sup>lt;sup>2</sup>S. Kim, T. Y. Chang, and J. O. Hirschfelder, Theoretical Chemistry Institute (University of Wisconsin) Rept. No. 40, March 1964; J. Chem. Phys. 43, 1092 (1965).

separable into two equations:

$$\begin{bmatrix} -2(\lambda^{2}-1) \left(F_{1}^{\prime\prime}+\{\left[2\lambda/(\lambda^{2}-1)\right]-Ra\}F_{1}^{\prime}\right)+2a\lambda R-4(\lambda R)-E^{(1)}R^{2}\lambda^{2}-\frac{1}{2}(a^{2}-b^{2})R^{2}\right]=C, \quad (9a)$$

$$\begin{bmatrix} -2(1-\mu^{2}) \left(F_{2}^{\prime\prime}+\{Rb \coth^{\frac{1}{2}}(Rb\mu)-\left[2\mu/(1-\mu^{2})\right]\}F_{2}^{\prime}\right) +2b\mu R \coth^{\frac{1}{2}}(Rb\mu)-\mu^{2\frac{1}{2}}R^{2}(a^{2}-b^{2})+E^{(1)}R^{2}\mu^{2}\right]=-C, \quad (9b)$$

in which the primes refer to differentiation with respect to the variable upon which  $F_1$  or  $F_2$  depends, and C is a separation constant at our disposal. C is chosen to ensure the proper behavior of  $F_1$  and  $F_2$  at the boundaries.

Equations (9a) and (9b) are integrable and we find after some rearrangement.

$$F_{1}(\lambda) = (RE^{(1)}/2a)\lambda + \{(E^{(1)}/a^{2}) + \lfloor (2-a)/a \rfloor\} \ln(\lambda+1) + F_{1}^{0}$$
(10a)

and

$$F_{2}(\mu) = A \ln\left[\sinh\frac{1}{2}(Rb\mu)/\mu\right] + \frac{1}{4}(ARb)\mu \coth\frac{1}{2}(Rb\mu) + \sum_{k=1}^{\infty} G(k) \ln\left[(4k^{2}\pi^{2} + R^{2}b^{2}\mu^{2})/(4k^{2}\pi^{2} + R^{2}b^{2})\right] \\ + B\left[(\mu \coth\frac{1}{2}Rb\mu) - (\coth Rb)\right](1-\mu^{2})^{-1}/(2Rb) + F_{2}^{0}, \quad (10b)$$

$$\begin{split} &A = (a^2 - b^2 - 2E^{(1)})/3b^2, \\ &B = -2E^{(1)}/a^2 - 4/a + 2Ra - 4R - (a^2 - b^2)/b^2 - 2RE^{(1)}/a - \frac{2}{3}R^2E^{(1)} + 2E^{(1)}/b^2 + \frac{1}{3}\left[R^2(a^2 - b^2)\right], \\ &G(k) = (R^2b^2 + 4k^2\pi^2)^{-1}\{B(4k^2\pi^2 - R^2b^2)/(4k^2\pi^2 + R^2b^2) + B + \frac{2}{3}R^2E^{(1)} - \frac{1}{3}\left[R^2(a^2 - b^2)\right]\}, \end{split}$$

in which  $F_1^0$  and  $F_2^0$  are constants of integration, which will be used to ensure that  $\psi^{(1)}$  is orthogonal to  $\psi^{(0)}$ . We have

$$E^{(1)} =$$

$$\frac{4R^{-2}\{(\sinh Rb/Rb)[(aR/2)+\frac{1}{4}-R-a^{-1}-(a^{2}/4b^{2})]+[\frac{1}{4}+(a^{2}/4b^{2})]\cosh Rb+R+a^{-1}+\frac{1}{12}(b^{2}-a^{2})R^{2}-aR-\frac{1}{2}\}}{\{[(2/aR)+2-(2/b^{2}R^{2})](\sinh Rb/Rb)+(2/R^{2}b^{2})\cosh Rb-[\frac{2}{3}+(2/aR)+(2/a^{2}R^{2})]\}}.$$
(11)

The second- and third-order perturbation energies are given by

$$E^{(2)} = \langle \psi^{(0)} | V | \psi^{(1)} \rangle / \langle \psi^{(0)} | \psi^{(0)} \rangle,$$
  

$$E^{(3)} = \langle \psi^{(1)} | V | \psi^{(1)} \rangle / \langle \psi^{(0)} | \psi^{(0)} \rangle.$$
(12)

These were evaluated by first integrating analytically over  $\lambda$  then integrating numerically over  $\mu$  using a 16-point Gaussian integration.

The expectation value of 5° with respect to a trial function of the form  $\phi = \psi^{(0)} + c \psi^{(1)}$  may be written as a function of C,  $\mathcal{E}_1(C)$ , accurate through third-order in the perturbation

$$\mathcal{E}_{1}(C) = (E^{(0)} + E^{(1)}) + \left[2CE^{(2)} + C^{2}(E^{(3)} - E^{(2)})/(1 + C^{2}S)\right],$$
(13)

where

$$S = \langle \psi^{(1)} | \psi^{(1)} \rangle / \langle \psi^{(0)} | \psi^{(0)} \rangle.$$
(14)

Minimizing  $\mathcal{E}_1(c)$  with respect to c gives

$$C_{\min} = (E^{(3)} - E^{(2)}) \pm \left[ (E^{(3)} - E^{(2)})^2 + 4(E^{(2)})^2 S \right]^{1/2} / 2E^{(2)} S$$
(15)

and then

$$\mathcal{E}_1(C = C_{\min}) = E^{(0)} + E^{(1)} + C_{\min}E^{(2)}.$$
(16)

In Table I, the electronic energy is given for R=0.1to R=9.0 a.u. The agreement with the exact answers of Bates, Ledsham, and Stewart<sup>3</sup> is very good.

above (that  $\psi^{(0)}$  does not approach the correct limiting form for  $R \rightarrow 0$ ) the perturbation series seems to be diverging for R < 1.0 a.u. For R = 0, we can solve the Small values of R: As expected from the comment perturbation equation, (7), and we find with

<sup>&</sup>lt;sup>3</sup> D. Bates, K. Ledsham, and A. Stewart, Phil. Trans. Roy. Soc. (London) A246, 215 (1953).

R	c(a.u.) — (	$E^{(0)} + E^{(1)})^{b}$ –	$\mathcal{E}_1(C=1)^{\circ}$	$-\epsilon_1(C_{\min})^d$	E <sup>e</sup> (Exact energy)
(	D.1 -	-0.41308 -	-0.27161 +	-0,48071(0,31979)	
(	0.2	0.42671	0.38287	0.48943(0.39634) -	+0.50268
(	0.4	0.45552	0.47095	0.50462(0.52225)	0.51079
(	0.6	0.48602	0.51006	0.52142(0.62459)	0.52431
(	0.8	0.51745	0.53747	0.54137(0.70546)	0.54274
1	1.0	0.54872	0.56278	0.56415(0.76733)	0.56481
1	1.2	0.57857	0.58778	0.58828(0.81325)	0.58861
1	1.4	0.60583	0.61173	0.61193 (0.84759)	0.61208
1	1.6	0.62966	0.63346	0.63354(0.87320)	0.63361
1	1.8	0.64966	0.65216	0.65219(0.89249)	0,65223
· · · · · · · · · · · · · · · · · · ·	2.0	0.66581	0.66750	0.66751(0.90732)	0.66754
4	2.2	0.67836	0.67954	0.67955(0.91890)	0.67956
2	2.4	0.68772	0.68856	0.68857(0.92815)	0.68858
2	2.6	0.69433	0.69495	0.69496(0.93530)	0.69496
2	2.8	0.69864	0.69911	0.69911(0.94137)	0.69911
3	3.0	0.70105	0.70142	0.70142(0.94644)	0.70143
3	3.2	0.70192	0.70221	0.70221(0.95049)	
3	3.4	0.70156	0.70179	0.70179(0.95401)	
3	3.5	0.70086	0.70121	0.70121(0.95352)	
3	3.6	0.70022	0.70041		
3	3.8	0.69811	0.69827		
4	1.0	0.69541	0.69555		0.69555
4	1.5	0.68695	0.68705		
5	5.0	0.67722	0.67729		0.67729
5	5.5	0.66714	0.66720		0.66719
6	5.0	0.65726	0.65731		0.65731
6	5.5	0.64786	0.64791		0.64791
7	7.0	0.63913	0.63913		0.63913
7	.5	0.63099	0.63103		0.63103
8	3.0	0.62357	0.62361		0.62361
8	3.5	0.61680	0.61683		0.61683
9	0.0	0.61063	0.61065		0.61066

TABLE I. Electronic energy of the  $2p\sigma$  state of  $H_2^+$  as a function of internuclear distance R.<sup>a</sup>

<sup>a</sup> All values in atomic units.

and

<sup>b</sup> Minimized energy through first order in the perturbation. Taken from Ref. 2

<sup>e</sup> Energy through third order in the perturbation (using a and b from Ref.

$$\psi^{(0)} = \exp(-ar) \cos\theta ]$$
  
$$\psi^{(1)}(R=0) = \exp(-ar) \cos\theta [2 \ln r + (3a-2)r + c].$$
  
(17)

If we choose  $\langle \psi^{(0)} | \psi^{(1)} \rangle = 0$ , then

$$c = [3(2-3a)/2a] + 2(\gamma + \ln 2a - \frac{3}{2}),$$

where  $\gamma$  is Euler's constant ( $\gamma = 0.577 \cdots$ ). Then, we have

$$E^{(0)}(R=0) + E^{(1)}(R=0) = \frac{5}{2}a^2 - 2a \qquad (18)$$

$$E^{(2)}(R=0) = -\frac{29}{2}a^2 + 10a - 2, \qquad (19)$$

$$E^{(3)}(R=0) = 78a^2 - 48a + 8, \tag{20}$$

$$S(R=0) = (3/a^2) - (13/a) + \frac{31}{4} + \frac{2}{3}\pi^2.$$
 (21)

Minimizing  $E^{(0)} + E^{(1)}$  with respect to a gives  $a = \frac{2}{5}$ , and  $E^{(0)} + E^{(1)} = -0.4$  a.u.; but this value of a gives

$$\sum_{i=0}^{8} E^{(i)}(a=0.4) = +0.56.$$
 (22)

Minimizing  $\mathcal{E}_1(C=1)$  with respect to a, gives  $a \approx 0.3$  and

2). See Eq. (13) of text, with c=1. <sup>d</sup> Energy through third order with minimization with respect to c. See Eq. (16) of text (values of cmin in parentheses).

e See Ref. 3.

 $\mathcal{E}_1(C=1) = -0.323$  a.u. and

$$\sum_{i=0}^{3} E^{(i)}(a=0.3) = -0.06.$$
 (23)

In either case (a=0.3 or a=0.4),  $E^{(3)}$  is larger than  $E^{(2)}$  in absolute magnitude. This indicates that the series seems to be diverging. The reason for this lies undoubtedly in the choice of the zeroth-order wavefunction. The first-order function (17) corrects the zeroth-order by putting in a term proportional to  $r \exp(-ar) \cos\theta$  (the correct wavefunction at R=0), but still contains terms which cause difficulties at r=0.

From Table I, we can see that  $\mathcal{E}_{I}(C=1)$  is greater than  $E^{(0)} + E^{(1)} [= \varepsilon_1(C=0)]$  for R < 0.4 a.u., and less for  $R \leq 0.4$  a.u. which indicates that the perturbation series is beginning to diverge at  $R \sim 0.4$  a.u.

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