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## Perturbation Calculation of the Energy of the First Excited State (2po) of H2+

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## ADVERTISEMENT



# Perturbation Calculation of the Energy of the First Excited State (2pб) of $\mathrm{H}_{2}{ }^{+}$ <br> Robert Silbey* <br> Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin 

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#### Abstract

The electronic energy of the $2 p \sigma$ state of $\mathrm{H}_{2}{ }^{+}$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.


RECENTLY, ${ }^{1}$ a perturbation calculation to third order in energy has been carried out on the ground state of $\mathrm{H}_{2}{ }^{+}$starting with a simple zeroth-order function. In this note, we present a similar calculation on the $2 p \sigma$ state of $\mathrm{H}_{2}{ }^{+}$. In this calculation, the firstorder perturbation equation is solved, and the energy calculated to third-order.

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

$$
\begin{equation*}
\psi^{(0)}=N \exp \left(-\frac{1}{2} R a \lambda\right) \sinh \frac{1}{2}(R b \mu) \tag{1}
\end{equation*}
$$

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),
$R \lambda \equiv\left(r^{2}+r R \cos \theta+\frac{1}{4} R^{2}\right)^{1 / 2}+\left(r^{2}-r R \cos \theta+\frac{1}{4} R^{2}\right)^{1 / 2}$,
$R \lambda \rightarrow 2 r+O\left(R^{2}\right)$,
$R \mu \equiv\left(r^{2}+r R \cos \theta+\frac{1}{4} R^{2}\right)^{1 / 2}-\left(r^{2}-r R \cos \theta+\frac{1}{4} R^{2}\right)^{1 / 2}$,
$R \mu \rightarrow R \cos \theta+O\left(R^{3}\right)$.
Hence, we have upon expansion of $\sinh \frac{1}{2}(R b \mu)$, and keeping terms of order $R$ only,

$$
\psi^{(0)} \rightarrow R b N(R \rightarrow 0) \exp (-a r) \cos \theta .
$$

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

$$
\begin{equation*}
\psi^{(0)}(R=0) \sim \exp (-a r) \cos \theta \tag{2}
\end{equation*}
$$

This wavefunction is not the correct limiting form for $R=0$, since the $2 p$ 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 $R$.

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

$$
\begin{equation*}
\mathfrak{X}^{(0)}=T-\left(T \psi^{(0)} / \psi^{(0)}\right)+E^{(0)} \tag{3}
\end{equation*}
$$

or

$$
\begin{align*}
\mathcal{H}^{(0)}=-\frac{1}{2} \Delta- & (2 a / R)\left[\lambda /\left(\lambda^{2}-\mu^{2}\right)\right] \\
& -\frac{1}{2}\left(a^{2}-b^{2}\right)\left[\left(1-\mu^{2}\right) /\left(\lambda^{2}-\mu^{2}\right)\right] \\
& -\left[2 b \mu / R\left(\lambda^{2}-\mu^{2}\right)\right] \operatorname{coth} \frac{1}{2}(R b \mu) \tag{4}
\end{align*}
$$

and

$$
\begin{equation*}
E^{(0)}=-\frac{1}{2} a^{2} \tag{5}
\end{equation*}
$$

Kim and Chang ${ }^{2}$ have used a wavefunction of the type of (1) and have minimized the expectation value of $\mathfrak{H C}$ 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 $\mathbb{H}^{(0)}$ corresponding to the ground-state wavefunction. ${ }^{1}$ (They are not the same, of course).
The perturbation, $V$, is given by $\mathfrak{H}-\mathfrak{H}^{(0)}$ or

$$
\begin{array}{r}
V=\frac{-4 \lambda}{R\left(\lambda^{2}-\mu^{2}\right)}+\frac{2 a \lambda}{R\left(\lambda^{2}-\mu^{2}\right)}+\frac{1}{2}\left(a^{2}-b^{2}\right)\left(\frac{1-\mu^{2}}{\lambda^{2}-\mu^{2}}\right) \\
+\frac{2 b \mu}{R\left(\lambda^{2}-\mu^{2}\right)} \operatorname{coth} \frac{1}{2}(R b \mu) \tag{6}
\end{array}
$$

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

$$
\begin{equation*}
\left(\mathcal{H}^{(0)}-E^{(0)}\right) \psi^{(1)}+\left(V-E^{(1)}\right) \psi^{(0)}=0 \tag{7}
\end{equation*}
$$

in which

$$
E^{(1)}=\left\langle\psi^{(0)}\right| V\left|\psi^{(0)}\right\rangle /\left\langle\psi^{(0)} \mid \psi^{(0)}\right\rangle
$$

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

$$
\begin{equation*}
\psi^{(1)}=\left[F_{1}(\lambda)+F_{2}(\mu)\right] \psi^{(0)} \tag{8}
\end{equation*}
$$

where $F_{1}$ and $F_{2}$ depend only on the variable indicated. When (8) is substituted into (7), we find that (7) is

[^1]separable into two equations:
\[

$$
\begin{align*}
& {\left[-2\left(\lambda^{2}-1\right)\left(F_{1}^{\prime \prime}+\left\{\left[2 \lambda /\left(\lambda^{2}-1\right)\right]-R a\right\}\right.\right.}\left.\left.F_{1}{ }^{\prime}\right)+2 a \lambda R-4(\lambda R)-E^{(1)} R^{2} \lambda^{2}-\frac{1}{2}\left(a^{2}-b^{2}\right) R^{2}\right]=C,  \tag{9a}\\
& {\left[-2\left(1-\mu^{2}\right)\left(F_{2}{ }^{\prime \prime}+\left\{R b \operatorname{coth} \frac{1}{2}(R b \mu)-\left[2 \mu /\left(1-\mu^{2}\right)\right]\right\} F_{2}{ }^{\prime}\right)\right.} \\
&\left.+2 b \mu R \operatorname{coth} \frac{1}{2}(R b \mu)-\mu^{21} R^{2}\left(a^{2}-b^{2}\right)+E^{(1)} R^{2} \mu^{2}\right]=-C, \tag{9b}
\end{align*}
$$
\]

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.

$$
\begin{equation*}
F_{1}(\lambda)=\left(R E^{(1)} / 2 a\right) \lambda+\left\{\left(E^{(1)} / a^{2}\right)+[(2-a) / a]\right\} \ln (\lambda+1)+F_{1} 0 \tag{10a}
\end{equation*}
$$

and

$$
\begin{align*}
F_{2}(\mu)=A \ln \left[\sinh \frac{1}{2}(R b \mu) / \mu\right]+\frac{1}{4}(A R b) \mu \operatorname{coth}_{2}^{1}(R b \mu) & +\sum_{k=1}^{\infty} G(k) \ln \left[\left(4 k^{2} \pi^{2}+R^{2} b^{2} \mu^{2}\right) /\left(4 k^{2} \pi^{2}+R^{2} b^{2}\right)\right] \\
& +B\left[\left(\mu \operatorname{coth} \frac{1}{2} R b \mu\right)-(\operatorname{coth} R b)\right]\left(1-\mu^{2}\right)^{-1} /(2 R b)+F_{2},  \tag{10b}\\
A & =\left(a^{2}-b^{2}-2 E^{(1)}\right) / 3 b^{2}, \\
B & =-2 E^{(1)} / a^{2}-4 / a+2 R a-4 R-\left(a^{2}-b^{2}\right) / b^{2}-2 R E^{(1)} / a-\frac{2}{3} R^{2} E^{(1)}+2 E^{(1)} / b^{2}+\frac{1}{3}\left[R^{2}\left(a^{2}-b^{2}\right)\right], \\
G(k) & =\left(R^{2} b^{2}+4 k^{2} \pi^{2}\right)^{-1}\left\{B\left(4 k^{2} \pi^{2}-R^{2} b^{2}\right) /\left(4 k^{2} \pi^{2}+R^{2} b^{2}\right)+B+\frac{2}{3} R^{2} E^{(1)}-\frac{1}{3}\left[R^{2}\left(a^{2}-b^{2}\right)\right]\right\},
\end{align*}
$$

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

$$
\begin{align*}
& E^{(1)}=  \tag{11}\\
& \frac{4 R^{-2}\left\{(\sinh R b / R b)\left[(a R / 2)+\frac{1}{4}-R-a^{-1}-\left(a^{2} / 4 b^{2}\right)\right]+\left[\frac{1}{4}+\left(a^{2} / 4 b^{2}\right)\right] \cosh R b+R+a^{-1}+\frac{1}{12}\left(b^{2}-a^{2}\right) R^{2}-a R-\frac{1}{2}\right\}}{\left\{\left[(2 / a R)+2-\left(2 / b^{2} R^{2}\right)\right](\sinh R b / R b)+\left(2 / R^{2} b^{2}\right) \cosh R b-\left[\frac{2}{3}+(2 / a R)+\left(2 / a^{2} R^{2}\right)\right]\right\}}
\end{align*}
$$

have

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

$$
\begin{align*}
& E^{(2)}=\left\langle\psi^{(0)}\right| V\left|\psi^{(1)}\right\rangle /\left\langle\psi^{(0)} \mid \psi^{(0)}\right\rangle, \\
& E^{(3)}=\left\langle\psi^{(1)}\right| V\left|\psi^{(1)}\right\rangle /\left\langle\psi^{(0)} \mid \psi^{(0)}\right\rangle . \tag{12}
\end{align*}
$$

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

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

$$
\begin{equation*}
\varepsilon_{1}(C)=\left(E^{(0)}+E^{(1)}\right)+\left[2 C E^{(2)}+C^{2}\left(E^{(3)}-E^{(2)}\right) /\left(1+C^{2} S\right)\right], \tag{13}
\end{equation*}
$$

where

$$
\begin{equation*}
S=\left\langle\psi^{(1)} \mid \psi^{(1)}\right\rangle /\left\langle\psi^{(0)} \mid \psi^{(0)}\right\rangle \tag{14}
\end{equation*}
$$

Minimizing $\varepsilon_{1}(c)$ with respect to $c$ gives

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

and then

$$
\begin{equation*}
\varepsilon_{1}\left(C=C_{\min }\right)=E^{(0)}+E^{(1)}+C_{\text {min }} E^{(2)} . \tag{16}
\end{equation*}
$$

In Table I, the electronic energy is given for $R=0.1$ to $R=9.0$ a.u. The agreement with the exact answers of Bates, Ledsham, and Stewart ${ }^{3}$ is very good.

Small values of $R$ : As expected from the comment
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 perturbation equation, (7), and we find [with

[^2]Table I. Electronic energy of the $2 p \sigma$ state of $\mathrm{H}_{2}{ }^{+}$as a function of internuclear distance $R .^{a}$

| $R$ (a.u.) | $-\left(E^{(0)}+E^{(1)}\right)^{\text {b }}$ | $-\varepsilon_{1}(C=1)^{\circ}$ | $-\mathcal{E}_{1}\left(C_{\text {min }}\right)^{\mathrm{d}}$ | $\begin{gathered} -E^{e} \text { (Exact } \\ \text { energy) } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: |
| 0.1 | +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 |
| 1.0 | 0.54872 | 0.56278 | $0.56415(0.76733)$ | 0.56481 |
| 1.2 | 0.57857 | 0.58778 | $0.58828(0.81325)$ | 0.58861 |
| 1.4 | 0.60583 | 0.61173 | $0.61193(0.84759)$ | 0.61208 |
| 1.6 | 0.62966 | 0.63346 | $0.63354(0.87320)$ | 0.63361 |
| 1.8 | 0.64966 | 0.65216 | $0.65219(0.89249)$ | 0.65223 |
| 2.0 | 0.66581 | 0.66750 | $0.66751(0.90732)$ | 0.66754 |
| 2.2 | 0.67836 | 0.67954 | $0.67955(0.91890)$ | 0.67956 |
| 2.4 | 0.68772 | 0.68856 | $0.68857(0.92815)$ | 0.68858 |
| 2.6 | 0.69433 | 0.69495 | $0.69496(0.93530)$ | 0.69496 |
| 2.8 | 0.69864 | 0.69911 | 0.69911 (0.94137) | 0.69911 |
| 3.0 | 0.70105 | 0.70142 | 0.70142 (0.94644) | 0.70143 |
| 3.2 | 0.70192 | 0.70221 | $0.70221(0.95049)$ |  |
| 3.4 | 0.70156 | 0.70179 | $0.70179(0.95401)$ |  |
| 3.5 | 0.70086 | 0.70121 | $0.70121(0.95352)$ |  |
| 3.6 | 0.70022 | 0.70041 |  |  |
| 3.8 | 0.69811 | 0.69827 |  |  |
| 4.0 | 0.69541 | 0.69555 |  | 0.69555 |
| 4.5 | 0.68695 | 0.68705 |  |  |
| 5.0 | 0.67722 | 0.67729 |  | 0.67729 |
| 5.5 | 0.66714 | 0.66720 |  | 0.66719 |
| 6.0 | 0.65726 | 0.65731 |  | 0.65731 |
| 6.5 | 0.64786 | 0.64791 |  | 0.64791 |
| 7.0 | 0.63913 | 0.63913 |  | 0.63913 |
| 7.5 | 0.63099 | 0.63103 |  | 0.63103 |
| 8.0 | 0.62357 | 0.62361 |  | 0.62361 |
| 8.5 | 0.61680 | 0.61683 |  | 0.61683 |
| 9.0 | 0.61063 | 0.61065 |  | 0.61066 |

${ }^{\text {a }}$ All values in atomic units.
${ }^{b}$ Minimized energy through first order in the perturbation. Taken from Ref. 2.
${ }^{c}$ Energy through third order in the perturbation (using $a$ and $b$ from Ref.

$$
\begin{align*}
& \left.\psi^{(0)}=\exp (-a r) \cos \theta\right] \\
& \qquad \psi^{(1)}(R=0)=\exp (-a r) \cos \theta[2 \ln r+(3 a-2) r+c] . \tag{17}
\end{align*}
$$

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

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

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

$$
\begin{equation*}
E^{(0)}(R=0)+E^{(1)}(R=0)=\frac{5}{2} a^{2}-2 a \tag{18}
\end{equation*}
$$

and

$$
\begin{gather*}
E^{(2)}(R=0)=-\frac{29}{2} a^{2}+10 a-2,  \tag{19}\\
E^{(3)}(R=0)=78 a^{2}-48 a+8,  \tag{20}\\
S(R=0)=\left(3 / a^{2}\right)-(13 / a)+\frac{31}{4}+\frac{2}{3} \pi^{2} . \tag{21}
\end{gather*}
$$

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

$$
\begin{equation*}
\sum_{i=0}^{3} E^{(i)}(a=0.4)=+0.56 \tag{22}
\end{equation*}
$$

Minimizing $\varepsilon_{1}(C=1)$ with respect to $a$, gives $a \approx 0.3$ and
2). See Eq. (13) of text, with $c=1$,
d Energy through third order with minimization with respect to $c$. See Eq.
(16) of text (values of $c_{\text {min }}$ in parentheses).
e See Ref. 3 .

- See Ref. 3.
$\varepsilon_{1}(C=1)=-0.323$ a.u. and

$$
\begin{equation*}
\sum_{i=0}^{3} E^{(i)}(a=0.3)=-0.06 \tag{23}
\end{equation*}
$$

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 $r \exp (-a r) \cos \theta$ (the correct wavefunction at $R=0$ ), but still contains terms which cause difficulties at $r=0$.

From Table I, we can see that $\mathcal{E}_{1}(C=1)$ is greater than $E^{(0)}+E^{(1)}\left[=\mathcal{E}_{1}(C=0)\right]$ 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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