Diatomic Molecules with Large Angular Momentum in the Born–Oppenheimer Approximation

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Abstract

The standard Born–Oppenheimer approximation for a diatomic molecule yields an expansion in powers of ϵ for the bound state associated with a given electron energy level, a fixed vibrational quantum number n, and a fixed angular momentum quantum number l. The expansion parameter ϵ is the fourth root of the ratio of the electron mass divided by the mean nuclear mass. In this paper we present an explicit approximation whose errors are uniformly bounded by $C\,\epsilon^5$ whenever the angular momentum quantum number satisfies $l < \kappa\,\epsilon^{-3/2}$.

We apply our approximation to the H_2^+ and HD^+ ions and compare the results with published rotational–vibrational energies.

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1 Introduction

In the standard fourth order Born–Oppenheimer approximation for a diatomic molecule, one fixes the kth electron energy level, the nth vibrational level, and the angular momentum l. The approximation then yields an expression that agrees with an exact energy level $\mathcal{E}_{k,n,l}(\epsilon)$ of the molecule up to an error that is bounded by $K_{k,n,l}\,\epsilon^5$. The expansion parameter ϵ is the fourth root of the ratio of the electron mass to the mean nuclear mass.

In this paper we keep k and n fixed, but allow l to grow as ϵ is reduced. Our main result is an expression that agrees with $\mathcal{E}_{k,n,l}(\epsilon)$ up to an error that is bounded by $K'_{k,n}\,\epsilon^5$ for all l that satisfy $l < \kappa\,\epsilon^{-3/2}$. This estimate is summarized in (1.3) below and in Theorem 4.1.

We prove this result in three steps:

Step 1. We first consider the small $\hbar$ asymptotics for the low-lying eigenvalues of

$$-\frac{\hbar^2}{2}\frac{\partial^2}{\partial r^2} + V_C(r) \qquad \text{on} \qquad L^2((0,\,\infty),\,dr),$$

where $V_C(r) = V(r) + \dfrac{C}{2\,r^2}$. We assume that V is C^5 and has a unique global minimum at some positive value $r_0 > 0$, with second derivative $V^{(2)}(r_0) > 0$. We impose a Dirichlet boundary condition at $r = 0$, and assume that $\liminf\limits_{r\to\infty} V(r) > V(r_0)$. We prove that there exists $B > 0$, such that $C \in [0,\,B]$ implies that V_C has a unique global minimum at some $r_C > r_0$. Furthermore, if we fix $N > 0$ and restrict $n \le N$ and $C \in [0,\,B]$, then the nth eigenvalue $\mathcal{E}_n(C,\,\hbar)$ satisfies the uniform estimate

$$\begin{aligned}
&\Bigg|\, \mathcal{E}_n(C,\,\hbar) \;-\; V_C(r_C) \;-\; \left(n+\frac{1}{2}\right)\left(V_C^{(2)}(r_C)\right)^{1/2} \hbar \\
&\quad - \left(\frac{1+2n+2n^2}{32}\,\frac{V_C^{(4)}(r_C)}{V_C^{(2)}(r_C)} - \frac{11+30n+30n^2}{288}\left(\frac{V_C^{(3)}(r_C)}{V_C^{(2)}(r_C)}\right)^2\right)\hbar^2 \,\Bigg| \\
&\le\; K_{B,N}\;\hbar^{5/2},
\end{aligned} \tag{1.1}$$

Step 2. We next study the behavior of r_C and the derivatives $V^{(m)}(r_C)$, for small $C \ge 0$. We then replace C by $l(l+1)\hbar^2$ and study the small $\hbar$ asymptotics of the nth eigenvalue $\mathcal{E}_{n,l}(\hbar)$ of

$$-\frac{\hbar^2}{2}\frac{\partial^2}{\partial r^2} + \frac{l(l+1)\,\hbar^2}{2\,r^2} + V(r).$$

For fixed $\kappa_1 > 0$, we prove that for small $\hbar$ and all $l \le \kappa_1 \hbar^{-3/4}$, the energy level $\mathcal{E}_{n,l}(\hbar)$ satisfies

$$
\begin{aligned}
\Bigg| \; & \mathcal{E}_{n,l}(\hbar) \; - \; V(r_0) \\
- \; & \left(n + \frac{1}{2}\right) \; \left(V^{(2)}(r_0)\right)^{1/2} \quad \hbar \\
- \; & \frac{1}{2\, r_0^2} \quad l(l+1)\; \hbar^2 \\
- \; & \left(\frac{1 + 2n + 2n^2}{32} \; \frac{V^{(4)}(r_0)}{V^{(2)}(r_0)} \; - \; \frac{11 + 30n + 30n^2}{288} \; \left(\frac{V^{(3)}(r_0)}{V^{(2)}(r_0)}\right)^2 \right) \quad \hbar^2 \\
- \; & \left(n + \frac{1}{2}\right) \; \frac{3V^{(2)}(r_0) + r_0\, V^{(3)}(r_0)}{2\; r_0^4\; [V^{(2)}(r_0)]^{3/2}} \quad l(l+1)\; \hbar^3 \\
- \; & \frac{1}{2\; r_0^6\; V^{(2)}(r_0)} \quad [l(l+1)]^2\; \hbar^4 \\
- \; & \left(n + \frac{1}{2}\right) \frac{-57(V^{(2)}(r_0))^2 - 3r_0^2(V^{(3)}(r_0))^2 + 2r_0V^{(2)}(r_0)(-9V^{(3)}(r_0) + r_0V^{(4)}(r_0))}{8\; r_0^8\; [V^{(2)}(r_0)]^{7/2}} \; [l(l+1)]^2\; \hbar^5 \\
- \; & \frac{9\; V^{(2)}(r_0) \; + \; r_0\, V^{(3)}(r_0)}{6\; r_0^{10}\; [V^{(2)}(r_0)]^3} \quad [l(l+1)]^3\; \hbar^6 \\
- \; & \frac{-156(V^{(2)}(r_0))^2 - 3r_0(V^{(3)}(r_0))^2 + r_0V^{(2)}(r_0)(-36V^{(3)}(r_0) + r_0V^{(4)}(r_0))}{24\; r_0^{14}\; [V^{(2)}(r_0)]^5} \quad [l(l+1)]^4\; \hbar^8 \Bigg| \\
\le \; & K \;\; \hbar^{5/2}, \qquad (1.2)
\end{aligned}
$$

for some K.

Step 3. We use (1.2) with $\hbar$ replaced by ϵ^2 to obtain our Born–Oppenheimer result. In the notation introduced below, the full molecular Hamiltonian can be expressed as

$$
-\frac{\epsilon^4}{2}\frac{\partial^2}{\partial r^2} \; + \; \frac{\epsilon^4}{2\, r^2}\, L^2 \; + \; h(r,\, \theta,\, \phi) \; + \; \epsilon^4\, D(\epsilon),
$$

where L^2 is the usual angular momentum operator and $h(r,\, \theta,\, \phi)$ is the electron Hamiltonian. We denote the kth electron energy level by $V(r)$ and the corresponding electronic state by $\Phi(r,\, \theta,\, \phi,\, \cdot\,)$. We assume this level has a non-degenerate minimum at $r_0 > 0$, and that it is isolated from the rest of the spectrum of $h(r,\, \theta,\, \phi)$. Then we prove the existence of $\kappa > 0$, such that for small ϵ, any fixed n, and all $l \le \kappa\, \epsilon^{-3/2}$, we have

$$
\begin{aligned}
\Bigg| \; & \mathcal{E}_{k,n,l}(\epsilon) \; - \; V(r_0) \\
- \; & \left(n+\frac{1}{2}\right) \; \left(V^{(2)}(r_0)\right)^{1/2} \quad \epsilon^2 \\
- \; & \frac{1}{2\,r_0^2} \quad l(l+1)\;\epsilon^4 \\
- \; & \left(-\,\frac{1}{2}\;\langle \Phi,\, \frac{\partial^2 \Phi}{\partial r^2}\rangle\Big|_{r=r_0} \; + \; \frac{1}{2\,r_0^2}\;\langle \Phi,\, L^2\,\Phi\rangle\big|_{r=r_0} \; + \; \langle \Phi,\, D(0)\,\Phi\rangle\big|_{r=r_0} \right) \quad \epsilon^4 \\
- \; & \left(\frac{1+2n+2n^2}{32}\;\frac{V^{(4)}(r_0)}{V^{(2)}(r_0)} \; - \; \frac{11+30n+30n^2}{288}\;\left(\frac{V^{(3)}(r_0)}{V^{(2)}(r_0)}\right)^2 \right) \quad \epsilon^4 \\
- \; & \left(n+\frac{1}{2}\right) \; \frac{3V^{(2)}(r_0)+r_0\,V^{(3)}(r_0)}{2\;r_0^4\;[V^{(2)}(r_0)]^{3/2}} \quad l(l+1)\;\epsilon^6 \\
- \; & \frac{1}{2\;r_0^6\;V^{(2)}(r_0)} \quad [l(l+1)]^2\;\epsilon^8 \\
- \; & \left(n+\frac{1}{2}\right) \frac{-57(V^{(2)}(r_0))^2 - 3r_0^2(V^{(3)}(r_0))^2 + 2r_0V^{(2)}(r_0)(-9V^{(3)}(r_0)+r_0V^{(4)}(r_0))}{8\;r_0^8\;[V^{(2)}(r_0)]^{7/2}} \; [l(l+1)]^2\;\epsilon^{10} \\
- \; & \frac{9\;V^{(2)}(r_0) \; + \; r_0\,V^{(3)}(r_0)}{6\;r_0^{10}\;[V^{(2)}(r_0)]^3} \quad [l(l+1)]^3\;\epsilon^{12} \\
- \; & \frac{-156(V^{(2)}(r_0))^2 - 3r_0(V^{(3)}(r_0))^2 + r_0V^{(2)}(r_0)(-36V^{(3)}(r_0)+r_0V^{(4)}(r_0))}{24\;r_0^{14}\;[V^{(2)}(r_0)]^5} \quad [l(l+1)]^4\;\epsilon^{16} \;\Bigg| \\
\leq \; & K\;\epsilon^5, \qquad (1.3)
\end{aligned}
$$

for some K. The precise result is stated in Theorem 4.1.

Remarks 1. The idea that there should be expansions of this type for large angular momenta goes back to Dunham [5], whose work is described in Herzberg's book [10]. No error estimates are presented in those references.

2. Many more details can be found in the Virginia Tech Ph.D. dissertation [11].

3. The only other mathematically rigorous work of which we are aware that handles large angular momentum is the article by Sordoni [18]. She proves the existence of expansions to all orders in powers of ϵ under the more restrictive assumption $l < \epsilon^{-1}$. She does not

present explicit energy formulas.

4. The first rigorous results for the time–independent Born–Oppenheimer approximation were those of [2, 4]. They proved the validity of the expansion through order ϵ^4 for fixed k, n, and l. Expansions to all orders were proved in [6] under the assumption that the potentials were smooth. The expansion to all orders in ϵ was extended to Coulomb potentials for diatomic molecules in [7], and for polyatomic molecules in [13]. By using optimal truncation of the series, approximations with errors of order $\exp(-c/\epsilon^2)$ were proved under analyticity assumptions on the potentials in [8, 9] when the nuclei had only one degree of freedom.

5. We place smoothness assumptions on the resolvent of the electron Hamiltonian that are not satisfied if the potentials between the particles are Coulomb potentials. We believe the techniques of [7, 13] would yield the same large angular momentum formulas in the Coulomb case, but proving that would be extremely technical. We note that even in the Coulomb case, $V(r)$ is analytic [12]. In the final section of the paper, we present comparisons between the results from our formulas and published energy levels for the H_2^+ and HD^+ ions, which, of course, have Coulomb potentials.

6. Semiclassical expansions for fixed n and l were first proved in [3, 17]. Optimal truncation of these expansions to yield approximations with errors of order $\exp(-c/\hbar)$ were obtained by Toloza [19, 20].

7. If one keeps l bounded by a constant, then the usual fourth order approximation is

$$\begin{aligned}\mathcal{E}_{k,n,l} \;\approx\; & V(r_0) \;+\; \left(n+\frac{1}{2}\right)\left(V^{(2)}(r_0)\right)^{1/2}\;\epsilon^2 \;+\; \frac{1}{2\,r_0^2}\;l(l+1)\,\epsilon^4 \\ & +\; \left(\frac{1+2n+2n^2}{32}\,\frac{V^{(4)}(r_0)}{V^{(2)}(r_0)} - \frac{11+30n+30n^2}{288}\left(\frac{V^{(3)}(r_0)}{V^{(2)}(r_0)}\right)^2\right)\;\epsilon^4 \\ & +\; \left(-\frac{1}{2}\,\langle\Phi,\,\frac{\partial^2\Phi}{\partial r^2}\rangle\Big|_{r=r_0} + \frac{1}{2\,r_0^2}\,\langle\Phi,\,L^2\,\Phi\rangle\big|_{r=r_0} + \langle\Phi,\,D(0)\,\Phi\rangle|_{r=r_0}\right)\;\epsilon^4.\end{aligned}$$

In the order presented here, these have the interpretation of the electron energy at the optimal nuclear configuration, the harmonic vibrational energy, the rotational energy, the first anharmonic vibrational corrections, and the diagonal Born–Oppenheimer correction.

8. It is trivial to extend the result (1.3) to allow $n \le N$ and $l \le \kappa\,\epsilon^{-3/2}$. In formula (1.3), one can see the coupling of rotations and vibrations of the molecule since there are terms that involve $(n+\frac{1}{2})\,l(l+1)$ and $(n+\frac{1}{2})\,[l(l+1)]^2$.

2 Uniform Semiclassical Estimates for V_C

This section is devoted to proving estimate (1.1). The crucial idea is to show that $\{ V_C \,:\, C \in [0,\, B] \}$ is a compact subset of a Banach space X of C^5 functions.

We assume $V \in C^5((0,\, \infty))$ has a local minimum at $r_0 > 0$, and that the second derivative $V^{(2)}(r_0)$ is strictly positive. By explicitly calculating derivatives of $V_C(r) = V(r) + \dfrac{C}{2\, r^2}$, we see that there exists $B > 0$, such that V_C has a minimum at $r_C \geq r_0$, such that r_C depends smoothly on C and $V_C^{(2)}(r_C) > 0$ whenever $C \in [0,\, B]$. By shrinking B if necessary, we can assume $r_C \in (a,\, b)$, where $0 < a < b < \infty$.

Definition Let X denote the space of C^5 functions on $[a,\, b] \subset (0,\, \infty)$, such that

$$\| f \|_X \;=\; \sum_{j=0}^{5} \| f^{(j)} \|_{L^\infty([a,\, b])}$$

is finite.

Lemma 2.1 *For V_C as above, the mapping $C \mapsto V_C$ is continuous from $[0,\, B]$ into X. Thus, its image is compact, and $\| V_C^{(j)} \|_{L^\infty([a,\, b])}$ is uniformly bounded for $C \in [0,\, B]$ and $j = 0,\, \cdots,\, 5$.*

Proof: The continuity follows from explicitly computing the form of V_C and its first five derivatives. ■

Because we make no assumption on the growth of V or its derivatives as r tends to 0 or ∞, we introduce a cut-off function $F_C(r) = F(r - r_C)$. We take F to be C^∞ with compact support, such that $F_C(r) = 1$ for $|r - r_C| < \delta$ and $F_C(r) = 0$ for $|r - r_C| > 2\delta$, where $\delta > 0$ is chosen so that the support of F_C is contained in $(a,\, b)$ whenever $C \in [0,\, B]$.

We now employ the following strategy to prove (1.1): For each fixed $C \in [0,\, B]$, we expand V_C in its fourth order Taylor series around r_C, and study the operator

$$\begin{aligned} &- \frac{\hbar^2}{2}\, \frac{\partial^2}{\partial r^2} \;+\; \left[V(r_C) \,+\, \frac{C}{2\, r_C^2} \right] \;+\; \frac{1}{2} \left[V^{(2)}(r_C) \,+\, \frac{3\, C}{r_C^4} \right] \, (r - r_C)^2 \\ &+\; \frac{1}{6} \left[V^{(3)}(r_C) \,-\, \frac{12\, C}{r_C^5} \right] \, (r - r_C)^3 \;+\; \frac{1}{24} \left[V^{(4)}(r_C) \,+\, \frac{60\, C}{r_C^6} \right] \, (r - r_C)^4. \end{aligned} \tag{2.1}$$

We apply formal perturbation theory to this operator defined on the whole real line. After completing the perturbation calculations, we multiply the formal approximate eigenfunctions

by the cut-off function F_C to obtain rigorous quasimodes for the original operator. We then use the results of [17] to see that the nth quasimode approximates the nth lowest eigenvalue. We obtain the uniformity for $C \in [0,\, B]$ as a consequence of Lemma 2.1.

To study the eigenvalue equation for (2.1) it is convenient to subtract $E_0 \;=\; V(r_C) \,+\, \dfrac{C}{2\, r_C^2}$ and to change variables from r to

$$y \;=\; A_C^{1/4}\; (r - r_C)/\epsilon,$$

where

$$A_C \;=\; V^{(2)}(r_C) \,+\, \frac{3\, C}{r_C^4}.$$

We divide the eigenvalue equation by $\hbar\, A_C^{1/2}$. This leads us to study the eigenvalue problem

$$\left(-\,\frac{1}{2}\,\frac{\partial^2}{\partial y^2} \;+\; \frac{1}{2}\, y^2 \;+\; \frac{\hbar^{1/2}\, A_C^{-5/4}}{6}\, \left[V^{(3)}(r_C) \,-\, \frac{12\, C}{r_C^5} \right]\, y^3 \right. \tag{2.2}$$

$$\left. +\;\; \frac{\hbar\, A_C^{-3/2}}{24}\, \left[V^{(4)}(r_C) \,+\, \frac{60\, C}{r_C^6} \right]\, y^4 \,+\, \cdots \right)\, \Psi \;=\; \left(E_2 \,+\, \hbar^{1/2}\, E_3 \,+\, \hbar\, E_4 \,+\, \cdots \right)\, \Psi.$$

We expand $\Psi = \Psi_0 + \hbar^{1/2}\Psi_1 + \hbar\Psi_2 + \cdots$, and equate terms of the same power of $\hbar^{1/2}$ in (2.2). Rather than normalizing Ψ, we require that each Ψ_j with $j \geq 1$ be orthogonal to Ψ_0. At each order one sees that this condition can be fulfilled, and that it imposes uniqueness on the Ψ_j for $j \geq 1$.

0th Order. The $\hbar^0$ terms require

$$\left(-\,\frac{1}{2}\,\frac{\partial^2}{\partial y^2} \;+\; \frac{1}{2}\, y^2 \right)\, \Psi_0 \;=\; E_2\, \Psi_0.$$

The eigenvalues are $E_2 = (n + 1/2)$ for $n = 0,\, 1,\, 2,\, \cdots$ and the normalized eigenfunctions are

$$\Psi_0 \;=\; \pi^{-1/4}\; 2^{-n/2}\; (n!)^{-1/2}\; H_n(y)\; e^{-y^2/2}.$$

1st Order. After some rearranging, the $\hbar^{1/2}$ terms now require

$$\left(-\,\frac{1}{2}\,\frac{\partial^2}{\partial y^2} \;+\; \frac{1}{2}\, y^2 \;-\; E_2 \right)\, \Psi_1 \;+\; \frac{A_C^{-5/4}}{6}\, \left[V^{(3)}(r_C) \,-\, \frac{12\, C}{r_C^5} \right]\, y^3\, \Psi_0 \;=\; E_3\, \Psi_0.$$

The left hand side of this equation is orthogonal to Ψ_0, and the right hand side is a multiple of Ψ_0. Thus, both sides are zero, and we have

$$E_3 \;=\; 0,$$

and

$$\Psi_1 \;=\; -\left(-\frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}y^2 - E_2\right)_r^{-1} \frac{A_C^{-5/4}}{6}\left[V^{(3)}(r_C) - \frac{12\,C}{r_C^5}\right] y^3\,\Psi_0,$$

where $\left(-\frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}y^2 - E_2\right)_r^{-1}$ denotes the reduced resolvent operator, *i.e.*, the inverse of the restriction of $\left(-\frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}y^2 - E_2\right)$ to vectors orthogonal to Ψ_0.

2nd Order. The $\hbar^1$ terms now require

$$\left(-\frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}y^2 - E_2\right)\Psi_2 + \frac{A_C^{-5/4}}{6}\left[V^{(3)}(r_C) - \frac{12\,C}{r_C^5}\right] y^3\,\Psi_1$$
$$+\; \frac{A_C^{-3/2}}{24}\left[V^{(4)}(r_C) + \frac{60\,C}{r_C^6}\right] y^4\,\Psi_0 \;=\; E_4\,\Psi_0.$$

The first term on the left hand side is orthogonal to Ψ_0, so if we take the inner product with Ψ_0, we learn that

$$E_4 \;=\; \left\langle \Psi_0,\; \frac{A_C^{-5/4}}{6}\left[V^{(3)}(r_C) - \frac{12\,C}{r_C^5}\right] y^3\,\Psi_1\right\rangle$$
$$+\; \left\langle \Psi_0,\; \frac{A_C^{-3/2}}{24}\left[V^{(4)}(r_C) + \frac{60\,C}{r_C^6}\right] y^4\,\Psi_0\right\rangle.$$

By expressing y^3 and y^4 in terms of raising and lowering operators and using the explicit form for the reduced resolvent, we can evaluate these inner products to obtain

$$E_4 \;=\; -\;\frac{11+30n+30n^2}{288}\,A_C^{-5/2}\left(V_C^{(3)}(r_C)\right)^2 \;+\; \frac{1+2n+2n^2}{32}\,A_C^{-3/2}\,V_C^{(4)}(r_C),$$

where $V_C^{(3)}(r_C) = V^{(3)}(r_C) - \frac{12\,C}{r_C^5}$ and $V_C^{(4)}(r_C) = V^{(4)}(r_C) + \frac{60\,C}{r_C^6}$.

Multiplying by $\hbar\,A^{1/2}$ we see that formally, the nth eigenvalue for the Hamiltonian (2.1) should equal

$$V_C(r_C) \;+\; \hbar\left(V_C^{(2)}(r_C)\right)^{1/2}\left(n+\frac{1}{2}\right) \tag{2.3}$$
$$+\; \hbar^2\left(\frac{1+2n+2n^2}{32}\,\frac{V_C^{(4)}(r_C)}{V_C^{(2)}(r_C)} - \frac{11+30n+30n^2}{288}\left(\frac{V_C^{(3)}(r_C)}{V_C^{(2)}(r_C)}\right)^2\right) + O\left(\hbar^{5/2}\right).$$

The main result of this section is that the $O\left(\hbar^{5/2}\right)$ error term in this expression is uniform for $C \in [0,\,B]$ and $n \le N$.

Theorem 2.2 *Suppose $V \in C^5((0,\,\infty))$ has a unique global minimum at r_0. Suppose $V^{(2)}(r_0) > 0$ and that $\liminf_{r\to 0} V(r) > V(r_0)$ and $\liminf_{r\to\infty} V(r) > V(r_0)$. There exists a positive value of B, such that $V_C(r) = V(r) + \frac{C}{2r^2}$ has a unique global minimum $r_C > r_0$, $V_C^{(2)}(r_C) > 0$ and $\liminf_{r\to\infty} V_C(r) > V_C(r_C)$ whenever $C \in [0,\,B]$. Furthermore, for any fixed N and sufficiently small $\hbar$, the operator*

$$-\,\frac{\hbar^2}{2}\,\frac{\partial^2}{\partial r^2} \;+\; V(r) \;+\; \frac{C}{2r^2}$$

has at least $N+1$ eigenvalues at the bottom of its spectrum. There exists $K_{B,N}$, such that the nth eigenvalue of

$$-\,\frac{\hbar^2}{2}\,\frac{\partial^2}{\partial r^2} \;+\; V(r) \;+\; \frac{C}{2\,r^2}$$

on $L^2((0,\,\infty))$ satisfies (1.1) whenever $C \in [0,\,B]$, $n \le N$, and $\hbar$ is sufficiently small.

Proof We have already commented that V_C has a global minimum at r_C for small C. The results about the $\liminf$'s are easy to verify for small C. By the implicit function theorem applied to the derivative $V'(r) - \dfrac{C}{r^3}$, we see that r_C is a smooth function of C.

For given $n = 0,\,1,\,2,\,\cdots$, we construct approximate eigenfunctions

$$\psi \;=\; F_C(r)\,\left(\Psi_0\left(\frac{A_C^{1/4}(r-r_C)}{\hbar^{1/2}}\right) + \hbar^{1/2}\,\Psi_1\left(\frac{A_C^{1/4}(r-r_C)}{\hbar^{1/2}}\right) + \hbar\,\Psi_2\left(\frac{A_C^{1/4}(r-r_C)}{\hbar^{1/2}}\right)\right)$$

with the corresponding approximate eigenvalues given by (2.3). We then substitute these into the two sides of the eigenvalue equation and estimate the difference. This rather tedious task is presented explicitly in [11], and for the sake of brevity, we only describe the details here.

We rewrite the potential V_C in its fourth order Taylor series around r_C plus the remainder. By standard estimates, on the support of F_C, the remainder is bounded by the maximum of $|V^{(5)}(r)|$ on the support of F_C times $(r-r_C)^5/5!$. Because of the scaling in $\hbar$, the norm of $(r-r_C)^5\,\psi(r)$ is bounded by a constant times $\hbar^{5/2}$ for $C \in [0,\,B]$ and fixed n. This bounds the contribution from the remainder term.

When any derivatives in the Hamiltonian act on $F_C(r)$, they produce terms that are of order $O\left(e^{-c/\hbar}\right)$. This is due to the rapid fall–off of the functions Ψ_j when $\frac{A_C^{1/4}(r-r_C)}{\hbar^{1/2}}$ becomes large. When $\hbar$ is small, the derivatives of F_C are non-zero only where this quantity is large.

The terms from the kinetic energy which do not involve derivaties of F_C and the Taylor series terms from the potential are precisely the ones that entered our formal perturbation

calculations. The choices of Ψ_j for $j = 0, 1, 2$ and the E_j for $j = 2, 3, 4$ force all terms of order $\hbar^{k/2}$ to cancel whenever $k \leq 4$. Thus, for each sufficiently small C and sufficiently small $\hbar$, it follows that the approximate eigenfunctions are quasimodes of the Hamiltonian with $O(\hbar^{5/2})$ errors. Since the Hamiltonian is self-adjoint, this implies that there is spectrum within an $O(\hbar^{5/2})$ distance of the approximate eigenvalue. That the spectrum nearby is discrete and that there are no other eigenvalues follow from the techniques of [17]. (The results of [17] apply on the whole real line with a growth assumption on the potential. The only difference here is that we introduce the cut–off function and insist on uniform estimates in C.) For fixed n, the uniformity of the error estimate for small C follows from the smoothness of all relevant quantities as functions of C and the compactness of the interval $[0, B]$.

The uniformity in n then follows because there are only finitely many values $n = 0, 1, 2, \cdots, N$. ■

Due to the presence of the cut off functions, this theorem and its proof extend to the situation where V is only defined in a neighborhood of r_0 and is increasing when $r > r_0$ and decreasing when $r < r_0$.

3 Rewriting the expansion in terms of $\mathbf{r_0}$

We now do the second step in our analysis. The estimate (1.1) contains terms that depend on r_C. We show that if $C = l(l+1)\,\hbar^2$ and $l \leq \kappa_1 \hbar^{-3/4}$, then (1.1) can be replaced by (1.2). Note that the restriction on l forces C to be bounded by a constant times $\hbar^{1/2}$, so it is small.

Proposition 3.1 *Assume the hypotheses of Theorem 2.2, and set $C = l(l+1)\,\hbar^2$, where $l \leq \kappa_1\,\hbar^{-3/4}$. Fix N and restrict $n \leq N$. Then the eigenvalue $\mathcal{E}_{n,l}$ of Theorem 2.2 satisfies the estimate (1.2).*

Proof We have already noted that r_C depends smoothly on C by the implicit function theorem. It thus has a Taylor series expansion

$$r_C \;=\; r_0 \;+\; a_1\,C \;+\; a_2\,C^2 \;+\; \cdots$$

We substitute this into the equation

$$V_C'(r_C) \;=\; 0, \qquad \text{where} \qquad V_C(r) \;= V(r) \;+\; \frac{C}{2\,r^2}.$$

We further expand V in its Taylor series around r_0, and then recursively determine the coefficients a_j. This yields

$$\begin{aligned} a_1 &= \frac{1}{r_0^3\, V^{(2)}(r_0)}, \\ a_2 &= -\,\frac{6\, V^{(2)}(r_0) \;+\; r_0\, V^{(3)}(r_0)}{2\; r_0^7\; (V^{(2)}(r_0))^3}, \\ a_3 &= \frac{90\,(V^{(2)}(r_0))^2 \;+\; 27\, r_0\, V^{(3)}(r_0) \;+\; 3\, r_0^2\,(V^{(3)}(r_0))^2 \;-\; r_0^2\, V^{(2)}(r_0)\, V^{(4)}(r_0)}{6\; r_0^{11}\; (V^{(2)}(r_0))^5}. \end{aligned}$$

In the notation we used for the perturbation expansion, the estimate (1.1) states

$$\Big|\, \mathcal{E}_n(C,\, \hbar) \;-\; E_0(C) \;-\; A_C^{1/2}\, E_2(C)\, \hbar \;-\; A_C^{1/2}\, E_4(C)\, \hbar^2 \,\Big| \;\le\; K_{B,n}\, \hbar^{5/2}.$$

Using the calculations above, we expand $E_0(C) = V(r_C) + \dfrac{C}{2\, r_C^2}$ to fourth order in C and make an error that is bounded by a constant times C^5. We expand $A_C^{1/2}\, E_2(C)$ through second order and make an error that is bounded by a constant times C^3. We similarly approximate $A_C^{1/2}\, E_4(C)$ by its zeroth order Taylor series in C and make an error that is bounded by a constant times C.

When $C = l(l+1)\,\hbar^2$ and $l \le \kappa_1\, \hbar^{-3/4}$, $C \in [0,\, B]$ for any B, as long as $\hbar$ is small. Thus, the conclusions of Theorem 2.2 apply. By replacing $E_0(C)$, $A_C^{1/2}\, E_2(C)$, and $A_C^{1/2}\, E_4(C)$ by their expansions, we obtain the estimate (1.2), since we make another error that is uniformly bounded by a constant times $\hbar^{5/2}$ when $C = l(l+1)\hbar^2$ is bounded by a constant times $\hbar^{1/2}$. ■

4 The Born–Oppenheimer Result

We now turn to the discussion of diatomic molecules, which requires some preliminary kinematical technicalities.

Consider a system of two nuclei of masses $\epsilon^{-4}\, M_1$ and $\epsilon^{-4}\, M_2$, together with $N-2$ electrons whose masses are 1. The full Hamiltonian for this system is

$$\widetilde{H}(\epsilon) \;=\; -\,\frac{\epsilon^4}{2\, M_1}\, \Delta_{X_1} \;-\; \frac{\epsilon^4}{2\, M_2}\, \Delta_{X_2} \;-\; \sum_{j=3}^{N} \frac{1}{2}\, \Delta_{X_j} \;+\; \sum_{i<j} V_{ij}(|X_i - X_j|).$$

Here $X_j \in \mathbb{R}^3$ denotes the position of the jth particle, Δ_{X_j} denotes the Laplacian in X_j, and the potential V_{ij} depends only on the distance between the ith and j^{th} particles.

To remove the center of mass motion, we use a particular set of clustered Jacobi coordinates [16]. We let $\xi_1 = X_2 - X_1$ denote the vector from the first nucleus to the second. We let $\xi_2 = X_4 - X_3$ denote the vector from the first electron to the second. We then let $\xi_3 = X_5 - \frac{1}{2}(X_4 + X_3)$ denote the vector from the center of mass of the first two electrons to the third, etc. In general, $\xi_j = X_{j+2} - \frac{1}{j-1} \sum_{i=3}^{j+1} X_i$. Finally, we let ζ denote the vector from the center of mass of the nuclei to the center of mass of the electrons.

In this coordinate system, the Hamiltonian we obtain by removing the center of mass motion from $\widetilde{H}(\epsilon)$ is

$$H(\epsilon) \;=\; -\,\frac{\epsilon^4}{2\,\mu_1}\,\Delta_{\xi_1} \;-\; \frac{1}{2\,\nu(\epsilon)}\,\Delta_\zeta \;-\; \sum_{j=2}^{N-2} \frac{1}{2\,\mu_j}\,\Delta_{\xi_j} \;+\; V(\xi_1,\,\xi_2,\,\cdots,\,\xi_{N-2},\,\zeta).$$

In this expression, the reduced mass $\nu(\epsilon)$ has a limit as ϵ tends to zero. We denote this limit by ν, and define

$$D(\epsilon) \;=\; \epsilon^{-4}\,\left(\frac{1}{2\,\nu(\epsilon)} - \frac{1}{2\,\nu}\right)\,\Delta_\zeta.$$

We can then write $H(\epsilon)$ as

$$H(\epsilon) \;=\; -\,\frac{\epsilon^4}{2\,\mu_1}\,\Delta_{\xi_1} \;+\; h(\xi_1) \;+\; \epsilon^4\,D(\epsilon).$$

Here, the electronic Hamiltonian

$$h(\xi_1) \;=\; -\,\frac{1}{2\,\nu}\,\Delta_\zeta \;-\; \sum_{j=2}^{N-2} \frac{1}{2\,\mu_j}\,\Delta_{\xi_j} \;+\; V(\xi_1,\,\xi_2,\,\cdots,\,\xi_{N-2},\,\zeta)$$

depends parametrically on ξ_1 and is independent of ϵ.

By rescaling ξ_1, we may assume $\mu_1 = 1$. We use spherical coordinates $(r,\,\theta,\,\phi)$ for the rescaled ξ_1, and we multiply the wave function by r. Slightly abusing notation, $H(\epsilon)$ takes the final form

$$H(\epsilon) \;=\; -\,\frac{\epsilon^4}{2}\,\frac{\partial^2}{\partial r^2} \;+\; \frac{\epsilon^4}{2\,r^2}\,L^2 \;+\; h(r,\,\theta,\,\phi) \;+\; \epsilon^4\,D(\epsilon),$$

where L^2 denotes the usual angular momentum operator.

Note that the θ and ϕ dependence of $h(r,\,\theta,\,\phi)$ is just a rotation that is implemented in the electron Hilbert space $L^2(\mathbb{R}^{3(N-2)},\; d\xi_2\,d\xi_3\,\cdots\,d\xi_{N-2}\,d\zeta)$ by a unitary transformation. Thus, any discrete eigenvalues of $h(r,\,\theta,\,\phi)$ depend only on r.

We henceforth assume that $h(r,\,\theta,\,\phi)$ satisfies the following hypotheses:

H1. We assume the resolvent of $h(r,\,\theta,\,\phi)$ is a C^5 function for $r \in (0,\,\infty)$.

H2. In an open neighborhood of some $r_0 > 0$, we assume $h(r,\,\theta,\,\phi)$ has a simple discrete eigenvalue $V(r)$ that has its minimum at r_0 and has $V''(r_0) > 0$.

Since $h(r,\,\theta,\,\phi)$ is a real differential operator, the eigenvector $\Phi(r,\,\theta,\,\phi,\,z)$ associated with $V(r)$ can be chosen to be real and normalized in $L^2(\mathbb{R}^{3(N-2)},\,dz)$, where we have let $z = (\xi_2,\,\xi_3,\,\cdots,\,\xi_{N-2},\,\zeta)$ denote the electron variables. We shall frequently drop the z dependence in the notation so that the electron eigenvalue equation is

$$h(r,\,\theta,\,\phi)\;\Phi(r,\,\theta,\,\phi) \;=\; V(r)\;\Phi(r,\,\theta,\,\phi).$$

Note that Hypotheses **H1** and **H2** imply that $V(r)$ is a C^5 function in a neighborhood of r_0. The reduced resolvent, $[h(r,\,\theta,\,\phi) - V(r)]_r^{-1}$, *i.e.*, the inverse of the restriction of $[h(r,\,\theta,\,\phi) - V(r)]$ to the subspace orthogonal to $\Phi(r,\,\theta,\,\phi)$, is also C^5 for r in the neighborhood of r_0.

We now apply the results of the previous sections with $\hbar$ replaced by ϵ^2 to see that if $C = l(l+1)\,\epsilon^4$ and $l \le \kappa_1\,\epsilon^{-3/2}$, there exists $\widetilde{K} > 0$, such that

$$\left\| \left(-\,\frac{\epsilon^4}{2}\,\frac{\partial^2}{\partial r^2} \;+\; \frac{\epsilon^4\,l(l+1)}{2\,r^2} \;+\; V(r) \;-\; E_{TS} \right)\,\psi \right\| \;\le\; \widetilde{K}\;\epsilon^5,$$

where, using earlier notation,

$$\psi \;=\; F_C(r)\;\left(\Psi_0\left(\tfrac{A^{1/4}(r-r_C)}{\epsilon}\right) \;+\; \epsilon\;\Psi_1\left(\tfrac{A^{1/4}(r-r_C)}{\epsilon}\right) \;+\; \epsilon^2\;\Psi_2\left(\tfrac{A^{1/4}(r-r_C)}{\epsilon}\right) \right),$$

and

$$\begin{aligned}
E_{TS} \;=\; & V(r_0) \;+\; \left(n+\frac{1}{2}\right)\,\left(V^{(2)}(r_0)\right)^{1/2}\;\epsilon^2 \;+\; \frac{1}{2\,r_0^2}\;l(l+1)\;\epsilon^4 \\
+\; & \left(\frac{1+2n+2n^2}{32}\,\frac{V^{(4)}(r_0)}{V^{(2)}(r_0)} \;-\; \frac{11+30n+30n^2}{288}\,\left(\frac{V^{(3)}(r_0)}{V^{(2)}(r_0)}\right)^2 \right)\;\epsilon^4 \\
+\; & \left(n+\frac{1}{2}\right)\,\frac{3V^{(2)}(r_0)+r_0\,V^{(3)}(r_0)}{2\;r_0^4\;[V^{(2)}(r_0)]^{3/2}}\;l(l+1)\;\epsilon^6 \;+\; \frac{1}{2\;r_0^6\;V^{(2)}(r_0)}\;[l(l+1)]^2\;\epsilon^8 \\
+\; & \left(n+\frac{1}{2}\right)\,\frac{-57(V^{(2)}(r_0))^2 - 3r_0^2(V^{(3)}(r_0))^2 + 2r_0V^{(2)}(r_0)(-9V^{(3)}(r_0)+r_0V^{(4)}(r_0))}{8\;r_0^8\;[V^{(2)}(r_0)]^{7/2}}\;[l(l+1)]^2\;\epsilon^{10} \\
+\; & \frac{9\;V^{(2)}(r_0)\;+\;r_0\,V^{(3)}(r_0)}{6\;r_0^{10}\;[V^{(2)}(r_0)]^3}\;[l(l+1)]^3\;\epsilon^{12}
\end{aligned}$$

$$+ \quad \frac{-156(V^{(2)}(r_0))^2 - 3r_0(V^{(3)}(r_0))^2 + r_0V^{(2)}(r_0)(-36V^{(3)}(r_0) + r_0V^{(4)}(r_0))}{24\, r_0^{14}\, [V^{(2)}(r_0)]^5} \quad [l(l+1)]^4\, \epsilon^{16}.$$

We let $Y_{l,m}$ denote the usual spherical harmonic $Y_{l,m}(\theta,\, \phi)$, and we let $Q = Q(r,\, \theta,\, \phi)$ denote the projection onto the subspace orthogonal to Φ in the electron Hilbert space. Then we define five more quantities, the first four of which are familiar from [6]:

$$\Sigma = \psi(r)\, Y_{l,m}(\theta,\, \phi)\, \Phi(r,\, \theta,\, \phi,\, z),$$

$$\widetilde{E}_4 = -\frac{1}{2} \left\langle \Phi,\, \frac{\partial^2 \Phi}{\partial r^2} \right\rangle \Big|_{r=r_C} + \frac{1}{2\, r_C^2} \left\langle \Phi,\, L^2\, \Phi \right\rangle \Big|_{r=r_C},$$

$$\psi_3^{\perp} = \epsilon\, \frac{\partial \psi}{\partial r}\, Y_{l,m}\, [h(r,\, \theta,\, \phi) - V(r)]_r^{-1}\, \frac{\partial \Phi}{\partial r},$$

$$\begin{aligned} \psi_4^{\perp} = {} & \frac{1}{2}\, \psi\, Y_{l,m}\, [h(r,\, \theta,\, \phi) - V(r)]_r^{-1}\, Q \left(\frac{\partial^2 \Phi}{\partial r^2} - 2\, D(0)\, \Phi \right) \\ & - \frac{1}{r_C^2}\, \psi\, [h(r,\, \theta,\, \phi) - V(r)]_r^{-1}\, (L\, Y_{l,m}) \cdot (L\, \Phi) \\ & - \frac{1}{2\, r_C^2}\, \psi\, Y_{l,m}\, [h(r,\, \theta,\, \phi) - V(r)]_r^{-1}\, Q\, (L^2\, \Phi), \end{aligned}$$

$$\psi_{adj} = \epsilon^4 \left[-\frac{2(r - r_C)}{r_C^3} + \frac{3(r - r_C)^2}{r_C^4} \right] \psi\, [h(r,\, \theta,\, \phi) - V(r)]_r^{-1}\, (L\, Y_{l,m}) \cdot (L\, \Phi).$$

Remarks

1. The inner products in the definition of $\widetilde{E}$ are in the electronic Hilbert space.

2. The function ψ is $F_C(r)$ times functions of $(r - r_C)/\epsilon$. Thus, the derivative of ψ with respect to r contains exponentially small terms and terms that contain factors of ϵ^{-1}. This leads to the following observations:

3. The norm of $\psi_3^{\perp}$ is $O(1)$.

4. The first and last terms in $\psi_4^{\perp}$ are $O(1)$.

5. When $l \le \kappa\, \epsilon^{-3/2}$, $L\, Y_{l,m}$ is $O(\epsilon^{-3/2})$, so the second term in $\psi_4^{\perp}$ is $O(\epsilon^{-3/2})$.

6. When $l \le \kappa\, \epsilon^{-3/2}$, the norm of ψ_{adj} is $O(\epsilon^{7/2})$.

7. Because of the scaling of a harmonic oscillator state ϕ_k, the norm of $(r - r_C)\, \phi_k$ is $O(\epsilon)$.

8. The quantity $\widetilde{E}_4$ depends on r_C. However, by doing a zeroth order Taylor series in C,

it agrees with

$$\widetilde{\widetilde{E}}_4 \;=\; -\,\frac{1}{2}\,\left\langle \Phi,\, \frac{\partial^2 \Phi}{\partial r^2} \right\rangle\Big|_{r=r_0} \;+\; \frac{1}{2\,r_C^2}\;\left\langle \Phi,\, L^2\,\Phi \right\rangle\big|_{r=r_0}\,,$$

up to an $O(\epsilon)$ error.

9. Similarly, $\langle\, \Phi,\, D(0)\,\Phi\,\rangle$ depends on r_C via Φ. However, up to an $O(\epsilon)$ error, it equals

$$\widetilde{D} \;=\; \langle\, \Phi,\, D(0)\,\Phi\,\rangle\big|_{r=r_0}\,.$$

Theorem 4.1 *Assume Hypotheses* **H1** *and* **H2**. *Fix $N \geq 0$ and $\kappa \geq 0$, and restrict $n \leq N$ and $l \leq \kappa\,\epsilon^{-3/2}$. Then there exists M such that*

$$\Bigg\| \Bigg(-\,\frac{\epsilon^4}{2}\,\frac{\partial^2}{\partial r^2} \;+\; \frac{\epsilon^4}{2\,r^2}\,L^2 \;+\; h(r,\,\theta,\,\phi) \;+\; \epsilon^4\,D(\epsilon)$$

$$-\;\Big\{ E_{TS} \,+\, \epsilon^4\,\widetilde{\widetilde{E}}_4 \,+\, \epsilon^4\,\widetilde{D} \Big\}\Bigg)\;\left(\Sigma \,+\, \epsilon^3\,\psi_3^{\perp} \,+\, \epsilon^4\,\psi_4^{\perp} \,+\, \psi_{adj}\right)\Bigg\| \;\leq\; M\,\epsilon^5.$$

The norm of the quasimode $\Sigma + \epsilon^3\,\psi_3^{\perp} + \epsilon^4\,\psi_4^{\perp} + \psi_{adj}$ is $O(1)$, so as long as the quasimode energy $E_{TS} + \epsilon^4\,\widetilde{\widetilde{E}}_4 + \epsilon^4\,\widetilde{D}$ lies below the essential spectrum, it describes a bound state of the molecule. That bound state energy satisfies (1.3) since the norm of the resolvent of a self-adjoint operator is the reciprocal of the distance to the spectrum.

Proof: From Remarks 8 and 9 above, it is sufficient to prove this result with $\epsilon^4\,\widetilde{\widetilde{E}}_4 + \epsilon^4\,\widetilde{D}$ replaced by $\epsilon^4\,\widetilde{E}_4 + \epsilon^4\,\langle\, \Phi,\, D(0)\,\Phi\,\rangle$.

To make use of cancellations, we rewrite the operator

$$-\,\frac{\epsilon^4}{2}\,\frac{\partial^2}{\partial r^2} \;+\; \frac{\epsilon^4}{2\,r^2}\,L^2 \;+\; h(r,\,\theta,\,\phi) \;+\; \epsilon^4\,D(\epsilon) \;-\; \Big\{ E_{TS} \,+\, \epsilon^4\,\widetilde{E}_4 \,+\, \epsilon^4\,\langle\, \Phi,\, D(0)\,\Phi\,\rangle \Big\}$$

as

$$\begin{aligned} &\left[-\,\frac{\epsilon^4}{2}\,\frac{\partial^2}{\partial r^2} \;+\; \frac{\epsilon^4\,l(l+1)}{2\,r^2} \;+\; V(r) \;-\; E_{TS} \right] \\ &+\;\; \frac{\epsilon^4}{2\,r^2}\,\left[\, L^2 \,-\, l(l+1)\,\right] \\ &+\;\; [h(r,\,\theta,\,\phi) \,-\, V(r)] \;+\; \epsilon^4\,D(\epsilon) \;-\; \epsilon^4\,\widetilde{E}_4 \;-\; \epsilon^4\,\langle\, \Phi,\, D(0)\,\Phi\,\rangle. \end{aligned} \tag{4.1}$$

We then explicitly compute (4.1) applied to the quasimode $\Sigma + \epsilon^3 \psi_3^\perp + \epsilon^4 \psi_4^\perp + \psi_{adj}$. This results in a large number of terms. The terms which contain derivatives of $F_C(r)$ have exponentially small norms, so we omit them. The remaining terms are

$$\left(\left[-\frac{\epsilon^4}{2} \frac{\partial^2}{\partial r^2} + \frac{\epsilon^4 \, l(l+1)}{2\, r^2} + V(r) - E_{TS} \right] \psi \right) Y_{l,m} \, \Phi \tag{4.2}$$

$$- \quad \epsilon^4 \left(\frac{\partial \psi}{\partial r} \frac{\partial \Phi}{\partial r} \right) Y_{l,m} \tag{4.3}$$

$$- \quad \frac{\epsilon^4}{2} \, \psi \, Y_{l,m} \, \frac{\partial^2 \Phi}{\partial r^2} \tag{4.4}$$

$$+ \quad \frac{\epsilon^4}{r^2} \, \psi \, (L \, Y_{l,m}) \cdot (L \, \Phi) \tag{4.5}$$

$$+ \quad \frac{\epsilon^4}{2\, r^2} \, \psi \, Y_{l,m} \, L^2 \, \Phi \tag{4.6}$$

$$- \quad \epsilon^4 \, \widetilde{E}_4 \, \Sigma \tag{4.7}$$

$$+ \quad \left[-\frac{\epsilon^4}{2} \frac{\partial^2}{\partial r^2} + \frac{\epsilon^4 \, l(l+1)}{2\, r^2} + V(r) - E_{TS} \right] \epsilon^3 \, \psi_3^\perp \tag{4.8}$$

$$+ \quad \frac{\epsilon^4}{2\, r^2} \left[L^2 - l(l+1) \right] \epsilon^3 \, \psi_3^\perp \tag{4.9}$$

$$+ \quad \epsilon^4 \, Y_{l,m} \, \frac{\partial \psi}{\partial r} \frac{\partial \Phi}{\partial r} \tag{4.10}$$

$$- \quad \epsilon^7 \, \widetilde{E}_4 \, \psi_3^\perp \tag{4.11}$$

$$+ \quad \left[-\frac{\epsilon^4}{2} \frac{\partial^2}{\partial r^2} + \frac{\epsilon^4 \, l(l+1)}{2\, r^2} + V(r) - E_{TS} \right] \epsilon^4 \, \psi_4^\perp \tag{4.12}$$

$$+ \quad \frac{\epsilon^4}{2\, r^2} \left[L^2 - l(l+1) \right] \epsilon^4 \, \psi_4^\perp \tag{4.13}$$

$$+ \quad \frac{\epsilon^4}{2} \, \psi \, Y_{l,m} \, Q \, \frac{\partial^2 \Phi}{\partial r^2} \tag{4.14}$$

$$- \quad \psi \, Y_{l,m} \, Q \, (D(0) \, \Phi) \tag{4.15}$$

$$- \quad \frac{\epsilon^4}{r_C^2} \, \psi \, (L \, Y_{l,m}) \cdot (L \, \Phi) \tag{4.16}$$

$$- \quad \frac{\epsilon^4}{2\, r_C^2} \, \psi \, Y_{l,m} \, Q \, (L^2 \, \Phi) \tag{4.17}$$

$$- \quad \epsilon^8 \, \widetilde{E}_4 \, \psi_4^{\perp} \tag{4.18}$$

$$+ \quad \left[- \frac{\epsilon^4}{2} \frac{\partial^2}{\partial r^2} + \frac{\epsilon^4 \, l(l+1)}{2\, r^2} + V(r) - E_{TS} \right] \psi_{adj} \tag{4.19}$$

$$+ \quad \frac{\epsilon^4}{2\, r^2} \left[L^2 - l(l+1) \right] \psi_{adj} \tag{4.20}$$

$$+ \quad \epsilon^4 \left[\frac{2(r - r_C)}{r_C^3} - \frac{3(r - r_C)^2}{r_C^4} \right] \psi \, (L\, Y_{l,m}) \cdot (L\, \Phi) \tag{4.21}$$

$$- \quad \epsilon^4 \, \widetilde{E}_4 \, \psi_{adj} \tag{4.22}$$

$$+ \quad \epsilon^4 \, D(\epsilon) \, \Sigma \tag{4.23}$$

$$+ \quad \epsilon^4 \, D(\epsilon) \, \left(\epsilon^3 \, \psi_3^{\perp} + \epsilon^4 \, \psi_4^{\perp} + \psi_{adj} \right) \tag{4.24}$$

$$- \quad \epsilon^4 \, \langle \Phi, \, D(0) \Phi \rangle \, \Sigma \tag{4.25}$$

$$- \quad \epsilon^4 \, \langle \Phi, \, D(0) \Phi \rangle \, \left(\epsilon^3 \, \psi_3^{\perp} + \epsilon^4 \, \psi_4^{\perp} + \psi_{adj} \right) \tag{4.26}$$

It is beneficial to add and subtract the following terms from this expression:

$$\epsilon^4 \left(- \frac{1}{2} \langle \Phi, \, \frac{\partial^2 \Phi}{\partial r^2} \rangle + \frac{1}{2\, r^2} \langle \Phi, \, L^2 \, \Phi \rangle \right) \Sigma \tag{4.27}$$

$$+ \quad \frac{\epsilon^4}{2} \langle \Phi, \, \frac{\partial^2 \Phi}{\partial r^2} \rangle \, \Sigma \tag{4.28}$$

$$- \quad \frac{\epsilon^4}{2\, r^2} \langle \Phi, \, L^2 \, \Phi \rangle \, \Sigma \tag{4.29}$$

From the proofs of Theorem 1.1 and Proposition 1.2, the norm of (4.2) is $O(\epsilon^5)$. Terms (4.3) and (4.10) cancel one another. The sum of the terms (4.4), (4.14) and (4.28) is zero. Terms (4.11), (4.18), (4.22), (4.24) and (4.26) are at most $O(\epsilon^5)$ in norm.

The sum of terms (4.5), (4.16) and (4.21) is

$$\epsilon^4 \left(\frac{1}{r^2} - \frac{1}{r_C^2} \right) \psi \, (L\, Y_{l,m}) \cdot (L\, \Phi) + \epsilon^4 \left[\frac{2(r - r_C)}{r_C^3} - \frac{3(r - r_C)^2}{r_C^4} \right] \psi \, (L\, Y_{l,m}) \cdot (L\Phi)$$

We expand the $\frac{1}{r^2}$ in this expression to second order about r_C and then observe the cancellation of everything with norm larger than $O(\epsilon^5)$.

The sum of (4.6), (4.17) and (4.29) is

$$\frac{\epsilon^4}{2\, r^2} \, \psi \, Y_{l,m} \, (L^2 \, \Phi) - \frac{\epsilon^4}{2\, r_C^2} \, \psi \, Y_{l,m} \, Q \, (L^2 \, \Phi) - \frac{\epsilon^4}{2\, r^2} \langle \Phi, \, L^2 \, \Phi \rangle \, \psi \, Y_{l,m} \, \Phi.$$

Expanding the first and third terms in this expression about r_C to first order yields

$$\frac{\epsilon^4}{2\,r_C^2}\;\psi\;Y_{l,m}\;L^2\;\Phi\;-\;\frac{\epsilon^4}{2\,r_C^2}\;\psi\;Y_{l,m}\;Q\;(L^2\,\Phi)\;-\;\frac{\epsilon^4}{2\,r_C^2}\;\langle\Phi,\,L^2\,\Phi\rangle\;\psi\;Y_{l,m}\;\Phi \tag{4.30}$$

$$-\;\frac{\epsilon^4}{r_C^3}\,(r-r_C)\;\psi\;Y_{l,m}\;(L^2\,\Phi)\;+\;\frac{\epsilon^4}{r_C^3}\,(r-r_C)\;\langle\Phi,\,L^2\,\Phi\rangle\;\psi\;Y_{l,m}\;\Phi$$

The sum of the first three terms in (4.30) is zero. The remaining two terms are $O(\epsilon^5)$.

The sum of terms (4.7) and (4.27) is

$$-\;\epsilon^4\;\left(-\;\frac{1}{2}\;\langle\Phi,\,\frac{\partial^2\Phi}{\partial r^2}\rangle\Big|_{r=r_C}\;+\;\frac{1}{2\,r_C^2}\;\langle\Phi,\,L^2\,\Phi\rangle\Big|_{r=r_C}\right)\;\Sigma$$

$$+\;\epsilon^4\;\left(-\;\frac{1}{2}\;\langle\Phi,\,\frac{\partial^2\Phi}{\partial r^2}\rangle\;+\;\frac{1}{2\,r^2}\;\langle\Phi,\,L^2\,\Phi\rangle\right)\;\Sigma$$

Expanding $-\frac{1}{2}\,\langle\Phi,\,\frac{\partial^2\Phi}{\partial r^2}\rangle\;+\;\frac{1}{2\,r^2}\,\langle\Phi,\,L^2\,\Phi\rangle$ to first order about r_C in this expression yields:

$$-\;\epsilon^4\;\left(-\;\frac{1}{2}\;\langle\Phi,\,\frac{\partial^2\Phi}{\partial r^2}\rangle\Big|_{r=r_C}\;+\;\frac{1}{2\,r_c^2}\;\langle\Phi,\,L^2\,\Phi\rangle\Big|_{r=r_C}\right)\;\Sigma$$

$$+\;\epsilon^4\;\left(-\;\frac{1}{2}\;\langle\Phi,\,\frac{\partial^2\Phi}{\partial r^2}\rangle\Big|_{r=r_C}\;+\;\frac{1}{2\,r_C^2}\;\langle\Phi,\,L^2\Phi\rangle\Big|_{r=r_C}\right)\;\Sigma \tag{4.31}$$

$$+\;\epsilon^4\;(r-r_C)\;\left[\frac{\partial}{\partial r}\;\left(-\;\frac{1}{2}\;\langle\Phi,\,\frac{\partial^2\Phi}{\partial r^2}\rangle\;+\;\frac{1}{2\,r^2}\;\langle\Phi,\,L^2\,\Phi\rangle\right)\right]\Bigg|_{r=r_C}\;\Sigma$$

The first two terms of (4.31) cancel; the remaining term is $O(\epsilon^5)$.

By taking $V(r_0)$ and $\dfrac{\epsilon^4\,l(l+1)}{2\,r_0^2}$ out of the expression E_{TS}, term (4.8) can be written as

$$\left[-\;\frac{\epsilon^4}{2}\;\frac{\partial^2}{\partial r^2}\;+\;\frac{\epsilon^4\,l(l+1)}{2\,r^2}\;-\;\frac{\epsilon^4\,l(l+1)}{2\,r_0^2}\;+\;V(r)\;-\;V(r_0)\;+\;O(\epsilon^2)\right]\;\epsilon^3\;\psi_3^{\perp}.$$

Expanding $\dfrac{\epsilon^4\,l(l+1)}{2\,r^2}\;+\;V(r)$ about r_0 to first order causes all the terms with norm larger than $O(\epsilon^5)$ to cancel.

The term (4.9) can be expanded as follows:

$$\begin{aligned}\frac{\epsilon^7}{2\,r^2}\;\left[L^2-l(l+1)\right]\;\psi_3^{\perp}\;&=\;\frac{\epsilon^8\,l(l+1)}{2\,r^2}\;Y_{l,m}\;[h(r,\theta,\phi)-V(r)]_r^{-1}\;\frac{\partial\psi}{\partial r}\;\frac{\partial\Phi}{\partial r}\\&+\;\frac{\epsilon^8}{r^2}\;(L\,Y_{l,m})\;\cdot\;\left(L\;\left([h(r,\theta,\phi)-V(r)]_r^{-1}\;\frac{\partial\psi}{\partial r}\;\frac{\partial\Phi}{\partial r}\right)\right)\\&+\;\frac{\epsilon^8}{2\,r^2}\;Y_{l,m}\;L^2\;\left([h(r,\theta,\phi)-V(r)]_r^{-1}\;\frac{\partial\psi}{\partial r}\;\frac{\partial\Phi}{\partial r}\right)\\&-\;\frac{\epsilon^8\,l(l+1)}{2\,r^2}\;Y_{l,m}\;[h(r,\theta,\phi)-V(r)]_r^{-1}\;\frac{\partial\psi}{\partial r}\;\frac{\partial\Phi}{\partial r}\end{aligned}$$

The first and last terms on the right hand side cancel, leaving two terms that are at most $O(\epsilon^5)$ in norm.

When examining term (4.12), it is beneficial to express $\psi_4^\perp$ as

$$\psi \left\{ \frac{1}{2}\, Y_{l,m}\, [h(r,\theta,\phi) - V(r)]_r^{-1}\, Q\, \frac{\partial^2 \Phi}{\partial r^2} \;-\; \frac{1}{r_C^2}\, [h(r,\theta,\phi) - V(r)]_r^{-1}\, (L\, Y_{l,m}) \cdot (L\, \Phi) \right.$$
$$\left. -\; \frac{1}{2\, r^2}\, Y_{l,m}\, [h(r,\theta,\phi) - V(r)]_r^{-1}\, Q\, (L^2\, \Phi) \right\}$$

Denote the factor in the braces by G, and observe that G is $O(\epsilon^{-3/2})$ in norm. Then term (4.12) can be written as

$$\left(\epsilon^4 \left[-\frac{\epsilon^4}{2}\, \frac{\partial^2}{\partial r^2} \;+\; \frac{\epsilon^4\, l(l+1)}{2\, r^2} \;+\; V(r) \;-\; E_{TS} \right] \psi \right)\, G \;+\; \epsilon^4 \left(-\frac{\epsilon^4}{2}\, \frac{\partial \psi}{\partial r}\, \frac{\partial G}{\partial r} \;-\; \frac{\epsilon^4}{2}\, \psi\, \frac{\partial^2 G}{\partial r^2} \right)$$

As we have shown before, when the expression in square brackets acts on ψ, the result is $O(\epsilon^5)$ in norm. So overall, the above expression is at most $O(\epsilon^5)$ in norm.

The term (4.13) equals

$$\frac{\epsilon^8}{2\, r^2}\, \left[\, L^2 \;-\; l(l+1)\, \right]\, \psi_4^\perp$$
$$= \frac{\epsilon^8}{2\, r^2} \left[(L\, Y_{l,m}) \cdot L \left(\psi\, [h(r,\theta,\phi) - V(r)]_r^{-1}\, Q\, \frac{\partial^2 \Phi}{\partial r^2} \right) \right.$$
$$+\; \frac{1}{2}\, Y_{l,m}\, L^2 \left(\psi\, [h(r,\theta,\phi) - V(r)]_r^{-1}\, Q\, \frac{\partial^2 \Phi}{\partial r^2} \right)$$
$$-\; \frac{1}{r_C^2}\, L^2\, \left(\psi\, [h(r,\theta,\phi) - V(r)]_r^{-1} \right)\, \left((L\, Y_{l,m}) \cdot (L\, \Phi) \right)$$
$$-\; \frac{2}{r_C^2}\, \left(L\, \left(\psi\, [h(r,\theta,\phi) - V(r)]_r^{-1} \right) \right) \cdot \left(l(l+1)\, Y_{l,m}\, L\, \Phi \right)$$
$$-\; \frac{2}{r_C^2}\, \left(L\, \left(\psi\, [h(r,\theta,\phi) - V(r)]_r^{-1} \right) \right) \cdot \left(L\, Y_{l,m}\, L^2\, \Phi \right)$$
$$-\; \frac{1}{r_C^2}\, \psi\, [h(r,\theta,\phi) - V(r)]_r^{-1}\, \left(2\, l(l+1)\, Y_{l,m}\, L^2\, \Phi \;+\; (L\, Y_{l,m}) \cdot (L(L^2\, \Phi)) \right)$$
$$-\; \frac{1}{2\, r^2}\, (L\, Y_{l,m}) \cdot \left(L\, \left(\psi\, [h(r,\theta,\phi) - V(r)]_r^{-1}\, Q\, (L^2\, \Phi) \right) \right)$$
$$\left. -\; \frac{1}{2\, r^2}\, Y_{l,m}\, L^2\, \left(\psi\, [h(r,\theta,\phi) - V(r)]_r^{-1}\, Q\, (L^2\, \Phi) \right) \right]$$

Of the terms in the square brackets on the right hand side, the one with largest norm is $O(\epsilon^{-3})$. Since the entire expression is multiplied by ϵ^8, this term is $O(\epsilon^5)$ in norm.

Term (4.19) can be rewritten as

$$\left[-\frac{\epsilon^4}{2}\frac{\partial^2}{\partial r^2} + \frac{\epsilon^4\, l(l+1)}{2\, r^2} - \frac{\epsilon^4\, l(l+1)}{2\, r_0^2} + V(r) - V(r_0) + O(\epsilon^2) \right] \psi_{adj}$$

by taking the appropriate terms out of E_{TS}. The second derivative with respect to r acting on ψ_{adj} can be expanded as

$$\begin{aligned}
& -\frac{\epsilon^4}{2}\frac{\partial^2}{\partial r^2}\,\psi_{adj} \\
= \quad & -\frac{\epsilon^8}{2}\left(\frac{\partial^2}{\partial r^2}\left[\frac{2(r-r_C)}{r_C^3} - \frac{3(r-r_C)^2}{r_C^4}\right]\right)\psi\ \left[h(r,\theta,\phi)-V(r)\right]_r^{-1}\ (L\,Y_{l,m})\cdot(L\,\Phi) \\
& -\frac{\epsilon^8}{2}\frac{\partial}{\partial r}\left[\frac{2(r-r_C)}{r_C^3} - \frac{3(r-r_C)^2}{r_C^4}\right]\frac{\partial}{\partial r}\left(\psi\ \left[h(r,\theta,\phi)-V(r)\right]_r^{-1}\ (L\,Y_{l,m})\cdot(L\,\Phi)\right) \\
& -\frac{\epsilon^8}{2}\left[\frac{2(r-r_C)}{r_C^3} - \frac{3(r-r_C)^2}{r_C^4}\right]\frac{\partial^2}{\partial r^2}\left(\psi\ \left[h(r,\theta,\phi)-V(r)\right]_r^{-1}\ (L\,Y_{l,m})\cdot(L\,\Phi)\right)
\end{aligned}$$

Each of these terms is at most $O(\epsilon^5)$ in norm. By expanding $\frac{\epsilon^4\, l(l+1)}{2\, r^2} + V(r)$ about r_0 as was done for (4.8), we see that the remaining terms of (4.19) are also $O(\epsilon^5)$ in norm.

Term (4.20) can be expanded as

$$\begin{aligned}
& \frac{\epsilon^4}{2\, r^2}\left[L^2 - l(l+1)\right]\psi_{adj} \\
= \quad & \frac{\epsilon^8}{2\, r^2}\, L^2\left(\left[h(r,\theta,\phi)-V(r)\right]_r^{-1}\left[\frac{2(r-r_C)}{r_C^3} - \frac{3(r-r_C)^2}{r_C^4}\right]\psi\right)(L\,Y_{l,m})\cdot(L\,\Phi) \\
& + \frac{\epsilon^8}{2\, r^2}\, L\left(\left[h(r,\theta,\phi)-V(r)\right]_r^{-1}\left[\frac{2(r-r_C)}{r_C^3} - \frac{3(r-r_C)^2}{r_C^4}\right]\psi\right) \\
& \qquad\qquad \times \left((L^2\,Y_{l,m})\,(L\,\Phi) + (L\,Y_{l,m})\,(L^2\,\Phi)\right) \\
& + \frac{\epsilon^8}{2\, r^2}\left[h(r,\theta,\phi)-V(r)\right]_r^{-1}\left[\frac{2(r-r_C)}{r_C^3} - \frac{3(r-r_C)^2}{r_C^4}\right]\psi \\
& \qquad\qquad \times \left((L^2\,Y_{l,m})\,(L\,\Phi) + (L\,Y_{l,m})\,(L^3\,\Phi)\right)
\end{aligned}$$

Again, each of these terms is at most $O(\epsilon^5)$ in norm.

Finally, by expanding $D(\epsilon)$ in ϵ in term (4.23), we see that the first term cancels with (4.25) and (4.15). The remaining terms are $O(\epsilon^5)$ in norm.

Since every term has norm at most $O(\epsilon^5)$, the theorem is proved. ■

5 Numerical Comparisons for H_2^+ and HD^+

In this section we present comparisons of our results with other published results for the H_2^+ and HD^+ ions. We selected these examples because the electron eigenvalue equation separates into three ordinary differential equations and they can be solved to exceptional accuracy. (See the end of this section for a summary of the details.)

We have chosen $V(r)$ to be the ground electron state. As a function of n and l, our results for $n \leq N$ and $l \leq \kappa\,\epsilon^{-3/2}$ yield the following approximation for the associated vibrational–rotational levels with an $O(\epsilon^5)$ error:

$$
\begin{aligned}
& V(r_0) \quad + \quad \left(V^{(2)}(r_0)\right)^{1/2} \left(n+\frac{1}{2}\right) \epsilon^2 \quad + \quad \frac{1}{2\,r_0^2} \quad l(l+1) \quad \epsilon^4 \\
& + \quad \left(\frac{1+2n+2n^2}{32} \, \frac{V^{(4)}(r_0)}{V^{(2)}(r_0)} \; - \; \frac{11+30n+30n^2}{288} \left(\frac{V^{(3)}(r_0)}{V^{(2)}(r_0)}\right)^2 \right) \quad \epsilon^4 \\
& + \quad \left(-\,\frac{1}{2} \, \langle \Phi, \, \frac{\partial^2 \Phi}{\partial r^2} \rangle \Big|_{r=r_0} \; + \; \frac{1}{2\,r_0^2} \, \langle \Phi, \, L^2\,\Phi \rangle \big|_{r=r_0} \; + \; \langle \Phi, \, D(0)\,\Phi \rangle |_{r=r_0} \right) \quad \epsilon^4 \\
& + \quad \frac{3V^{(2)}(r_0) + r_0\,V^{(3)}(r_0)}{2\;r_0^4\;[V^{(2)}(r_0)]^{3/2}} \quad \left(n+\frac{1}{2}\right) \; l(l+1)\;\epsilon^6 \\
& + \quad \frac{1}{2\;r_0^6\;V^{(2)}(r_0)} \quad [l(l+1)]^2\;\epsilon^8 \\
& + \quad \frac{-57(V^{(2)}(r_0))^2 - 3r_0^2(V^{(3)}(r_0))^2 + 2r_0V^{(2)}(r_0)(-9V^{(3)}(r_0) + r_0V^{(4)}(r_0))}{8\;r_0^8\;[V^{(2)}(r_0)]^{7/2}} \; \left(n+\frac{1}{2}\right) \; [l(l+1)]^2\;\epsilon^{10} \\
& + \quad \frac{9\;V^{(2)}(r_0) \; + \; r_0\,V^{(3)}(r_0)}{6\;r_0^{10}\;[V^{(2)}(r_0)]^3} \quad [l(l+1)]^3\;\epsilon^{12} \\
& + \quad \frac{-156(V^{(2)}(r_0))^2 - 3r_0(V^{(3)}(r_0))^2 + r_0V^{(2)}(r_0)(-36V^{(3)}(r_0) + r_0V^{(4)}(r_0))}{24\;r_0^{14}\;[V^{(2)}(r_0)]^5} \quad [l(l+1)]^4\;\epsilon^{16}.
\end{aligned}
$$

This expression can be written as a linear combination of the following quantities:

$$
1, \quad \left(n+\frac{1}{2}\right), \quad \left(n+\frac{1}{2}\right)^2, \quad l(l+1), \quad [l(l+1)]^2, \quad [l(l+1)]^3, \quad [l(l+1)]^4,
$$

$$
\left(n+\frac{1}{2}\right) \; l(l+1), \qquad \text{and} \qquad \left(n+\frac{1}{2}\right) \; [l(l+1)]^2.
$$

Since one is normally interested in transition energies and because terms that depend on the electron state Φ are hard to evaluate, we ignore the multiples of 1 in that linear combination.

They are

$$V(r_0) \;+\; \frac{1}{64}\,\frac{V^{(4)}(r_0)}{V^{(2)}(r_0)}\,\epsilon^4 \;-\; \frac{7}{576}\,\left(\frac{V^{(3)}(r_0)}{V^{(2)}(r_0)}\right)^2\,\epsilon^4$$

$$+\quad\left(-\,\frac{1}{2}\,\langle\Phi,\,\frac{\partial^2\Phi}{\partial r^2}\rangle\Big|_{r=r_0} \;+\; \frac{1}{2\,r_0^2}\,\langle\Phi,\,L^2\,\Phi\rangle\big|_{r=r_0} \;+\; \langle\Phi,\,D(0)\,\Phi\rangle\big|_{r=r_0}\right)\,\epsilon^4.$$

The following table lists coefficients of the remaining terms for the H_2^+ ion. The first column of coefficients is obtained from our formula. The second column of coefficients is obtained by a least squares fit of the energies with $0 \le n \le 3$ and $0 \le l \le 19$ given in the paper of Moss [15]. The third column of coefficients is from the NIST web site http://webbook.nist.gov/cgi/cbook.cgi?ID=C12184906&Units=SI&Mask=1000#Diatomic. All energies are expressed in wavenumbers (cm^{-1}), and $\cdots$ indicates that no number was given.

Table 1: Coefficient comparison for H_2^+

	Our Approximation	Fit of Data from [15]	NIST
$l(l+1)$	30.01570	29.7985	30.2
$[l(l+1)]^2$	0.01997	-0.01902	$\cdots$
$[l(l+1)]^3$	0.00001	0.00001	$\cdots$
$[l(l+1)]^4$	-2.4997×10^{-10}	-7.01838×10^{-9}	$\cdots$
$(n+\frac{1}{2})$	2326.63	2304.69	2321.7
$(n+\frac{1}{2})\,[l(l+1)]$	-1.7326	-1.45401	-1.685
$(n+\frac{1}{2})\,[l(l+1)]^2$	0.00361	0.00052	$\cdots$
$(n+\frac{1}{2})^2$	-76.199	-60.0183	-66.2

The next table lists the analogous data for the HD^+ ion. The first column of coefficients is obtained from our formula. The second column of coefficients is obtained by a least squares fit of the states with $0 \le n \le 3$ and $0 \le l \le 15$ listed in the paper of Moss [14]. The third

column of coefficients is from the NIST web site http://webbook.nist.gov/cgi/cbook.cgi?ID=C12181167&Units=SI&Mask=1000#Diatomic. All energies are expressed in wavenumbers (cm^{-1}), and $\cdots$ indicates that no number was given.

Table 2: Coefficient comparison for HD^+

	Our Approximation	Fit of Data from [14]	NIST
$l(l+1)$	22.5118	22.3958	22.45
$[l(l+1)]^2$	0.01509	-0.01088	$\cdots$
$[l(l+1)]^3$	1.6875×10^{-5}	6.08×10^{-6}	$\cdots$
$[l(l+1)]^4$	-3.0582×10^{-8}	-2.7551×10^{-9}	$\cdots$
$(n+\frac{1}{2})$	2007.81	2000.51	1913.1
$(n+\frac{1}{2})\,[l(l+1)]$	-1.03985	-0.96072	-1.00
$(n+\frac{1}{2})\,[l(l+1)]^2$	0.00274	0.00028	$\cdots$
$(n+\frac{1}{2})^2$	-57.196	-45.7563	$\cdots$

Although we shall not speculate on the discrepancies in some of these numbers, we are very skeptical of the NIST coefficient of 1913.1 for $(n+\frac{1}{2})$ for HD^+ since it disagrees with the other two results by roughly 5%. The NIST values for this coefficient in Tables 1 and 2 are not consistent with one another. Since they are the harmonic frequencies, the value in Table 2 should be $\sqrt{3/4}$ times the value in Table 1 because 3/4 is the ratio of the reduced masses of the nuclei. In fact, $2321.7 \times \sqrt{3/4} = 2010.7$. Furthermore, using Gaussian 2003 with the large aug-cc-pvqz basis set, we obtain 2007.3811.

Numerical Techniques

We conclude this section with a discussion of our numerical techniques for solving the electronic problem for these ions.

The electronic eigenvalue problems for H_2^+ and HD^+ are the same. It is well-known that they separate in elliptical coordinates.

Two of the coordinates are

$$\xi \;=\; \frac{r_1 \,+\, r_2}{R} \qquad 1 \,\leq\, \xi \,\leq\, \infty,$$

and

$$\eta \;=\; \frac{r_1 \,-\, r_2}{R} \qquad -\,1 \,\leq\, \eta \,\leq\, 1,$$

where R is the distance between the two nuclei and r_j is the distance from the electron to the jth nucleus. The third coordinate is ϕ, the angle of rotation about the internuclear axis.

In these coordinates, the Laplacian takes the form

$$\Delta \;=\; \frac{4}{R^2\,(\xi^2-\eta^2)}\,\left[\,\frac{\partial}{\partial\xi}\,(\xi^2-1)\,\frac{\partial}{\partial\xi} \;+\; \frac{\partial}{\partial\eta}\,(1-\eta^2)\,\frac{\partial}{\partial\eta}\,\right] \;+\; \frac{1}{R^2\,(\xi^2-1)\,(1-\eta^2)}\,\frac{\partial^2}{\partial\phi^2}$$

We set

$$\psi \;=\; X(\xi)\;Y(\eta)\;e^{i\Lambda\phi}$$

where Λ must be an integer. Since we are only interested in the ground electronic state, we have $\Lambda = 0$, and we can ignore ϕ. The functions $X(\xi)$ and $Y(\eta)$ satisfy

$$\frac{d}{d\xi}\,\left[\,(\xi^2-1)\,\frac{dX}{d\xi}\,\right] \;+\; \left(\,\frac{1}{2}\,E\,R^2\,\xi^2 \;+\; 2\,R\,\xi \;+\; A \;-\; \frac{\Lambda^2}{\xi^2-1}\,\right)\;X \;=\; 0 \tag{5.1}$$

$$\frac{d}{d\eta}\,\left[\,(1-\eta^2)\,\frac{dY}{d\eta}\,\right] \;+\; \left(\,-\,\frac{1}{2}\,E\,R^2\,\eta^2 \;-\; A \;-\; \frac{\Lambda^2}{1-\eta^2}\,\right)\;Y \;=\; 0, \tag{5.2}$$

where A is a separation constant. In our notation, $R = r$ and $E = V(r)$.

To solve (5.1) and (5.2) efficiently and accurately, we replace ξ by $w = \alpha(\xi - 1)$ and expand $X(\xi)$ in Laguerre polynomials in w times $\exp(-w/2)$. We choose $\alpha = 2\sqrt{-2E}$ to get the proper exponential fall off of $X(\xi)$. We expand $Y(\eta)$ in Legendre polynomials. For both expansions, we use polynomials of degrees up to 50, which is overkill. The expansions converge rapidly. We use an iterative root–finding procedure to determine E and the separation constant A for any given $R > 0$.

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