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On H_2^+ for small internuclear separation

Martin Klaus

Department of Mathematics, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

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Abstract. We study the behaviour of the electronic energy $E(R)$ of the hydrogen molecular ion as the internuclear separation R goes to zero. We prove that $E(R)$ is not analytic at $R=0$ and we find its expansion in terms of powers of R and $R^2 \ln R$ up to order $R^9(\ln R)^3$. This rigorously justifies earlier work by Byers Brown and Steiner. We also give an outline of how one can prove non-analyticity by means of a perturbation treatment based on the united atom.

1. Introduction

The Hamiltonian for the H_2^+ molecule reads (in atomic units)

$$H(R) = -\tfrac{1}{2}\Delta - |\boldsymbol{x} - \tfrac{1}{2}\boldsymbol{R}|^{-1} - |\boldsymbol{x} + \tfrac{1}{2}\boldsymbol{R}|^{-1} \qquad \boldsymbol{R} = (R, 0, 0). \tag{1.1}$$

Here $\boldsymbol{x}$ denotes the position of the electron. The two nuclei are located at $\pm\frac{1}{2}\boldsymbol{R}$, respectively. Let $E(R)$ denote the lowest eigenvalue of $H(R)$. In this paper we will take another look at the analytic behaviour of $E(R)$ near $R=0$. Our work is based on an earlier paper by Byers Brown and Steiner (1966) (henceforth denoted by BBS) who discovered the remarkable fact that $E(R)$ cannot be expanded in powers of R alone, but that logarithms must also be included. Explicitly,

$$E(R) = -2 + \tfrac{2}{3}(2R)^2 - \tfrac{2}{3}(2R)^3 + \tfrac{22}{135}(2R)^4 - \tfrac{2}{9}(2R)^5 \ln R + \mathrm{O}(R^5). \tag{1.2}$$

The numerical coefficient for R^5 is also known but, to our knowledge, no further terms have been calculated previously. The reason why we are not quite satisfied with this result is that it has never been justified rigorously. BBS obtain their expansion from what appears to be the initial step in an iterative process for finding successive approximations to $E(R)$. However, BBS do not prove convergence of this process and thus do not have rigorous control on the remainder. The determination of $E(R)$ is closely connected with the integration of two ordinary differential equations (equations (2.4) and (2.5)) which we get when we separate the Schrödinger equation in spheroidal coordinates. It turns out that only equation (2.5) causes problems and, indeed, this equation has been disputed in several earlier papers. Concerning this matter the reader is referred to the paper by Chakravarty (1939). Prior to BBS it was common practice to determine the separation constant in (2.5) from an implicit equation involving continued fractions. It is to the merit of BBS that an alternative method which is better suited for analytical purposes was proposed.

The chief goal of this paper is to give a rigorous justification of the method of BBS. This will be done in § 3 where we will prove convergence of the iterative process.

In § 2 we separate the variables and replace the Schrödinger equation by a set of two ordinary differential equations. We discuss some of their properties which will be needed later on.

In § 4 we expand $E(R)$ up to order $R^9(\ln R)^3$, thereby adding nine more terms to those already known. The point is that one only needs the first approximation in the iterative process to calculate these terms. This is a consequence of the error estimates derived in § 3. Furthermore, we state a conjecture concerning the general nature of the expansion for $E(R)$.

An alternative approach to our problem does exist which does not use separation of variables, namely the perturbation treatment based on the united atom. In fact, it was by this method that we were first able to show that $E(R)$ is non-analytic. We give a summary of our results in § 5.

Finally, we mention that our initial motivation for looking into H_2^+ for small nuclear separation was its relation to our recent work on coupling constant thresholds (Klaus and Simon 1980). For, by using scaling, $H(R)$ is unitarily equivalent to $R^{-2}\tilde{H}(R)$ where

$$\tilde{H}(R) = -\tfrac{1}{2}\Delta - R(|\boldsymbol{x} - \tfrac{1}{2}\boldsymbol{n}|^{-1} + |\boldsymbol{x} + \tfrac{1}{2}\boldsymbol{n}|^{-1}) \qquad \boldsymbol{n} = \boldsymbol{R}/R \tag{1.3}$$

and so, as $R \downarrow 0$, $\tilde{H}(R)$ represents a Schrödinger operator in the weak coupling limit. However, unlike Klaus and Simon (1980), the potential here is long-range. Therefore, we have a definite interest in knowing at least whether or not $E(R)$ is analytic.

2. Separation of variables

It is known that the Schrödinger equation

$$H_R\psi = E(R)\psi \tag{2.1}$$

may be separated in spheroidal coordinates ξ, η, ϕ, such that

$$\xi = (r_1 + r_2)/R \qquad (1 \leq \xi < \infty) \qquad \eta = (r_1 - r_2)/R \qquad (-1 \leq \eta \leq 1). \tag{2.2}$$

Here r_1 and r_2 denote the distances of the electron from the two nuclei and ϕ is the azimuthal angle about the axis joining the two nuclei. The ground-state wavefunction ψ is axially symmetric and can be written as

$$\psi = H(\eta)X(\xi). \tag{2.3}$$

Then H and X obey the 'inner' and 'outer' equations

$$[\mathrm{d}/\mathrm{d}\eta](1-\eta^2)(\mathrm{d}H/\mathrm{d}\eta) - p^2(1-\eta^2)H + CH = 0 \tag{2.4}$$

$$[\mathrm{d}/\mathrm{d}\xi](\xi^2-1)(\mathrm{d}X/\mathrm{d}\xi) + 2p(1+\sigma)\xi X - p^2(\xi^2-1)X - CX = 0. \tag{2.5}$$

The parameters p and σ are related to $E(R)$ and R as follows:

$$p^2 = -\tfrac{1}{2}R^2E(R) \tag{2.6}$$

$$1 + \sigma = R/p. \tag{2.7}$$

The limit $R \to 0$, $E(R) \to -2$ corresponds to the limit $p \to 0$, $\sigma \to 0$. The equation

$$C_{\text{inner}}(p) = C_{\text{outer}}(p, \sigma), \tag{2.8}$$

where C_{inner} and C_{outer} distinguish the values of the separation constant C as determined from (2.4) and (2.5) respectively, is to be regarded as an implicit equation for $\sigma(p)$. Once we know $\sigma(p)$ we can find $E(R)$ by means of (2.6) and (2.7). Lieb and Simon (1978) proved that $E(R)$ is a non-decreasing function of R. Hoffmann-Ostenhof (1980) proved strict monotonicity for $R>0$. When R is small, one can also find upper and lower bounds to $E(R)$ which show that $E(R)+2$ vanishes quadratically as $R\downarrow 0$. Grosse *et al* (1978) showed that

$$-2+\tfrac{1}{2}R^2+\mathrm{O}(R^3)\leqslant E\leqslant -2+\tfrac{8}{3}R^2+\mathrm{O}(R^3). \tag{2.9}$$

Thus, without loss the parameter σ may be assumed to be positive.

The properties of the inner equation are well known. We note that $C_{\text{inner}}(p)$ is analytic in a disc of radius approximately 3.17 (Guerrieri and Hunter 1982).

3. Construction of C_{outer}

We first consider C_{outer}. Following BBS (but replacing their variable ζ by x) we put

$$X(\xi)=\mathrm{e}^{-p\xi}(1+\xi)^{\sigma}F(x) \tag{3.1}$$

$$F(x)=1+\sigma^2 f(x) \tag{3.2}$$

$$x=(\xi-1)/(\xi+1) \qquad 0\leqslant x\leqslant 1. \tag{3.3}$$

Then equation (2.5) becomes an equation for f, namely

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(x\frac{\mathrm{d}f}{\mathrm{d}x}\right)+\left(\frac{-4p}{(1-x)^2}+\frac{2\sigma}{1-x}\right)\left(x\frac{\mathrm{d}f}{\mathrm{d}x}\right)+\frac{B}{(1-x)^2}-\frac{1}{1-x}=-\sigma^2\left(\frac{B}{(1-x)^2}-\frac{1}{1-x}\right)f \tag{3.4}$$

where

$$C_{\text{outer}}=\sigma(1+2p)+\sigma^2-\sigma^2 B. \tag{3.5}$$

We require that

$$f(0)=0 \tag{3.6}$$

and that f be bounded. Equation (3.4) will be solved by the method of successive approximations. To this end we set

$$f_0=0 \tag{3.7}$$

and

$$B_n=\int_0^1\frac{\mathrm{e}^{A(z)}}{1-z}(\sigma^2 f_{n-1}(z)+1)\,\mathrm{d}z\left(\int_0^1\frac{\mathrm{e}^{A(z)}}{(1-z)^2}(\sigma^2 f_{n-1}(z)+1)\,\mathrm{d}z\right)^{-1} \qquad n=1,2,\ldots \tag{3.8}$$

$$f_n(x)=\int_0^x\mathrm{d}z\,\frac{\mathrm{e}^{-A(z)}}{z}\int_z^1\mathrm{e}^{A(u)}\left(\frac{B_n}{(1-u)^2}-\frac{1}{1-u}\right)(\sigma^2 f_{n-1}(u)+1)\,\mathrm{d}u \qquad n=1,2,\ldots \tag{3.9}$$

where

$$A(x)=-4p/(1-x)-2\sigma\ln(1-x). \tag{3.10}$$

The idea behind these definitions is the following. Suppose f_{n-1} is known and bounded in x. Substituting f_{n-1} for f on the right-hand side of (3.4) and integrating we get

$$x\frac{\mathrm{d}f}{\mathrm{d}x}=\mathrm{e}^{-A(x)}\int_x^1 \mathrm{e}^{A(u)}\left(\frac{B}{(1-u)^2}-\frac{1}{1-u}\right)(\sigma^2 f_{n-1}(u)+1)\,\mathrm{d}u+d\,\mathrm{e}^{-A(x)} \tag{3.11}$$

where d is an arbitrary constant. The first term on the right-hand side of (3.11) turns out to be integrable at $x=1$ whereas $\mathrm{e}^{-A(x)}$ is non-integrable there. Thus, we set $d=0$. On dividing (3.11) by x and integrating such that $f(0)=0$, we obtain

$$f(x)=\int_0^x \frac{\mathrm{e}^{-A(z)}}{z}\int_z^1 \mathrm{e}^{A(u)}\left(\frac{B}{(1-u)^2}-\frac{1}{1-u}\right)(\sigma^2 f_{n-1}(u)+1)\,\mathrm{d}u \tag{3.12}$$

provided the z integral exists at $z=0$. Now we simply choose B such that this is the case. Setting

$$\int_0^1 \mathrm{e}^{A(u)}\left(\frac{B}{(1-u)^2}-\frac{1}{1-u}\right)(\sigma^2 f_{n-1}(u)+1)\,\mathrm{d}u=0 \tag{3.13}$$

and solving this equation for $B=B_n$ we obtain (3.8). Substituting B_n for B in (3.12) and calling the left-hand side f_n yields (3.9). This set-up constitutes a convenient mathematical formulation of the iterative process proposed by BBS. In contrast to BBS we avoid changing back to the variable ξ in order to find B. In the theorem below we will establish convergence of the sequences B_n and f_n. As an essential ingredient in the proof we will need a lower bound on p^σ. In other words we have to prevent p from getting arbitrarily small independently of σ. Therefore, it is convenient to introduce the set

$$G_\alpha=\{p,\sigma\,|\,0<p\leqslant \mathrm{e}^{-1/\alpha},\ 0\leqslant\sigma\leqslant|\ln p|^{-1}\} \tag{3.14}$$

where α is a positive constant on which further restrictions will be placed below. Note that $0\leqslant\sigma\leqslant\alpha$ in G_α and $G_{\alpha'}\subset G_\alpha$ if $\alpha'<\alpha$.

Theorem 3.1. Suppose $(p,\sigma)\in G_\alpha$ where α is sufficiently small. Then

(i) $$\lim_{n\to\infty} B_n(\sigma,p)=B(\sigma,p)=B \tag{3.15}$$

and

(ii) $$\lim_{n\to\infty} f_n(x)=f(x) \tag{3.16}$$

exist.

In (i) and (ii) convergence is uniform in G_α. In (ii) it is in addition uniform with respect to x. Moreover, the limiting function f together with the constant B satisfy the differential equation (3.4).

For the proof of the theorem we need some estimates which we will derive first. For $k=1,2$, we define

$$I_k=I_k(p,\sigma)=\int_{1/2}^1 \mathrm{d}z\,\frac{\mathrm{e}^{-A(z)}}{z}\int_z^1 \frac{\mathrm{e}^{A(u)}}{(1-u)^k}\,\mathrm{d}u. \tag{3.17}$$

Then we have the following proposition.

Proposition 3.2. If we let $\alpha = \frac{1}{4}$, then we can find positive constants c_1, c_2, d_1, d_2 such that

$$d_1|\ln p| \leq I_1 \leq c_1|\ln p| \tag{3.18}$$

and

$$d_2/p \leq I_2 \leq c_2/p \tag{3.19}$$

holds for all values $(p, \sigma) \in G_{1/4}$. Furthermore,

$$\int_0^1 \frac{e^{A(z)}}{(1-z)^k}\, dz = (4p)^{-2\sigma+1-k}\Gamma(2\sigma+k-1, 4p) \qquad (k=1,2) \tag{3.20}$$

where $\Gamma(y, x) = \int_x^\infty e^{-t}t^{y-1}\, dt$.

Proof. Let $\tilde{I}_k$ denote the integral having the same integrand as I_K but with the factor z^{-1} deleted. Since $\frac{1}{2} \leq z \leq 1$ we have $\tilde{I}_k \leq I_k \leq 2\tilde{I}_k$, so that it suffices to establish (3.18) and (3.19) when I_k is replaced by $\tilde{I}_k$. On making the substitutions $4p/(1-z) = x$, $4p/(1-u) = t$ we obtain

$$\tilde{I}_k = (4p)^{2-k} \int_{8p}^\infty dx\, e^x x^{-2-2\sigma} \int_x^\infty e^{-t} t^{2\sigma+k-2}\, dt. \tag{3.21}$$

To examine the singular behaviour of $\tilde{I}_k$ we restrict the variables x and t to the interval $[0, 1]$ and replace the exponentials by 1. This means we consider

$$\begin{aligned}\tilde{\tilde{I}}_K &= (4p)^{2-k} \int_{8p}^1 dx\, x^{-2-2\sigma} \int_x^1 t^{2\sigma+k-2}\, dt \\ &= \begin{cases} \dfrac{4p-\frac{1}{2}}{2\sigma+1} + \dfrac{(8p)^{-2\sigma}-1}{4\sigma(2\sigma+1)} & k=1 \\[2ex] \dfrac{1-(8p)^{2\sigma+1}}{(8p)^{2\sigma+1}(2\sigma+1)^2} + \dfrac{\ln 8p}{2\sigma+1} & k=2 \end{cases}\end{aligned} \tag{3.22}$$

(note that $8p < 1$ on $G_{1/4}$).
If $k = 1$ we observe that we can find $\beta_1, \beta_2 > 0$ such that

$$\beta_1 \leq [(8p)^{-2\sigma} - 1]/2\sigma|\ln 8p| \leq \beta_2 \tag{3.23}$$

for all $(p, \sigma) \in G_{1/4}$. Thus $\tilde{\tilde{I}}_1$ obeys bounds of the form (3.18). Similarly, if $k = 2$, we have $e^{-1} \leq p^\sigma \leq 1$ if $(p, \sigma) \in G_{1/4}$, showing that $\tilde{\tilde{I}}_2$ obeys bounds of the form (3.19). From these estimates the desired bounds for $\tilde{I}_k$, and thus I_k, follow in an obvious way. We omit the details.

The calculation leading to (3.20) is elementary. This proves the proposition.

Proof of theorem 3.1. The main effort goes into proving that the denominator in (3.8) is bounded away from zero uniformly in n. This will be done by establishing a suitable *a priori* bound on $\|f_n\|_\infty (\|f\|_\infty = \sup_{0 \leq x \leq 1} |f(x)|)$. In this proof K will be used to denote various constants whose precise value is unimportant to us. If we let $0 \leq x \leq \frac{1}{2}$ and assume $(p, \sigma) \in G_{1/4}$, then by virtue of (3.13) we may write

$$f_n(x) = -\int_0^x dz \frac{e^{-A(z)}}{z} \int_0^z e^{A(u)} \left(\frac{B_n}{(1-u)^2} - \frac{1}{1-u}\right)(\sigma^2 f_{n-1}(u) + 1)\, du. \tag{3.24}$$

Hence, it is obvious that

$$|f_n(x)| \leqslant K(|B_n|+1)(\sigma^2\|f_{n-1}\|_\infty+1). \tag{3.25}$$

Now let $\frac{1}{2} < x \leqslant 1$; then

$$f_n(x) = f_n(\tfrac{1}{2}) + \int_{1/2}^{x} dz\, \frac{e^{-A(z)}}{z} \int_z^1 e^{A(u)}\left(\frac{B_n}{(1-u)^2} - \frac{1}{1-u}\right)(\sigma^2 f_{n-1}(u)+1)\, du. \tag{3.26}$$

On estimating $f_n(\frac{1}{2})$ by (3.25) and the integral in (3.26) by means of proposition (3.2) we obtain

$$|f_n(x)| \leqslant K[(|B_n|/p) + |\ln p|](\sigma^2\|f_{n-1}\|_\infty + 1) \tag{3.27}$$

which is valid for all $x \in [0, 1]$.

Now suppose that

$$\sigma^2\|f_{n-1}\|_\infty < 1. \tag{3.28}$$

As we will see below, this is an allowable assumption. Then, by using (3.20) and (3.8), we obtain

$$|B_n| \leqslant 4p\, \frac{\Gamma(2\sigma, 4p)}{\Gamma(2\sigma+1, 4p)}\, \frac{1+\sigma^2\|f_{n-1}\|_\infty}{1-\sigma^2\|f_{n-1}\|_\infty}. \tag{3.29}$$

It is easy to see that $\Gamma(2\sigma+1, 4p) \geqslant K$ and $\Gamma(2\sigma, 4p) \leqslant K|\ln p|$ so that by substituting (3.29) in (3.27) and using (3.28) to simplify the result we obtain

$$\|f_n\|_\infty \leqslant K|\ln p|/(1-\sigma^2\|f_{n-1}\|_\infty). \tag{3.30}$$

Now we let $D(p) = K|\ln p|$ and define a function $g(x)$ by

$$g(x) = D(p)/(1-\sigma^2 x). \tag{3.31}$$

Then the equation

$$g(x) = x \tag{3.32}$$

has the two solutions

$$x_\pm = [1 \pm (1-4\sigma^2 D(p))^{1/2}]/2\sigma^2. \tag{3.33}$$

Suppose from now on, that in addition to being less than $\frac{1}{4}$, α has been chosen to be so small that $4\sigma^2 D(p) < 1$ if $(p, \sigma) \in G_\alpha$. Then, since $(1-x)^{1/2} \geqslant 1-x$ if $0 \leqslant x \leqslant 1$, we see that

$$x_- \leqslant 2D(p) = 2K|\ln p| \tag{3.34}$$

and

$$\sigma^2 x_- < 1. \tag{3.35}$$

Since $g'(x) > 0$ for $0 \leqslant x < \sigma^{-2}$ we conclude that

$$g^{[n]}(0) < x_- \tag{3.36}$$

where $g^{[n]}$ denotes the nth iterate of g. Moreover, $g^{[n]}(0) \uparrow x_-$ as $n \to \infty$.

Since $f_0 = 0$ by definition, (3.28) is satisfied for $n = 1$. Thus, by (3.30) and (3.36)

$$\|f_1\|_\infty \leqslant g(0) < x_-. \tag{3.37}$$

Hence, by virtue of (3.35), assumption (3.28) is again satisfied for $n = 2$. Hence

$$\|f_2\|_\infty \leqslant g(\|f_1\|_\infty) \leqslant g(g(0)) < x_- \tag{3.38}$$

$$\vdots$$

$$\|f_n\|_\infty \leqslant g^{[n]}(0) < x_-. \tag{3.39}$$

From this we infer that

$$\|f_n\|_\infty \leqslant 2K|\ln p| \tag{3.40}$$

for all $n \geqslant 1$. Moreover, by (3.29)

$$|B_n| \leqslant Kp|\ln p| \qquad n \geqslant 1. \tag{3.41}$$

To estimate the difference $f_n - f_{n-1}$, we use (3.24) if $0 \leqslant x \leqslant \frac{1}{2}$ and (3.26) if $\frac{1}{2} \leqslant x \leqslant 1$. By means of the estimate $\|B_n f_{n-1} - B_{n-1} f_{n-2}\|_\infty \leqslant |B_n - B_{n-1}| \|f_{n-2}\|_\infty + |B_n| \|f_{n-1} - f_{n-2}\|_\infty$ along with (3.18), (3.19), (3.40) and (3.41) we find that

$$\|f_n - f_{n-1}\|_\infty \leqslant K(\sigma^2 |\ln p| \|f_{n-1} - f_{n-2}\|_\infty + p^{-1}|B_n - B_{n-1}|) \tag{3.42}$$

where $n \geqslant 2$.

To estimate $B_n - B_{n-1}$ we write a_n (b_n) for the numerator (denominator) in (3.8). Then $B_n - B_{n-1} = (a_n - a_{n-1})b_n^{-1} + (b_{n-1} - b_n)a_{n-1}b_n^{-1}b_{n-1}^{-1}$ and since $|b_n^{-1}| \leqslant Kp$, $|b_n^{-1}b_{n-1}^{-1}| \leqslant Kp^2$, $|a_{n-1}| \leqslant K|\ln p|$, $|a_n - a_{n-1}| \leqslant K\sigma^2 |\ln p| \|f_{n-1} - f_{n-2}\|_\infty$ and $|b_n - b_{n-1}| \leqslant K\sigma^2 p^{-1} \|f_{n-1} - f_{n-2}\|_\infty$ we conclude that

$$|B_n - B_{n-1}| \leqslant Kp\sigma^2 |\ln p| \|f_{n-1} - f_{n-2}\|_\infty \qquad n \geqslant 2. \tag{3.43}$$

Substituting (3.43) in (3.42) yields

$$\|f_n - f_{n-1}\|_\infty \leqslant K\sigma^2 |\ln p| \|f_{n-1} - f_{n-2}\|_\infty. \tag{3.44}$$

For the rest of the proof the letter K will be used exclusively to denote the constant in (3.44) and we will use subscripts to denote any other constants. Iterating (3.44) gives

$$\|f_n - f_{n-1}\|_\infty \leqslant (K\sigma^2|\ln p|)^{n-1} \|f_1\|_\infty \leqslant K_1 |\ln p| (K\sigma^2 |\ln p|)^{n-1} \qquad n \geqslant 1 \tag{3.45}$$

where in the last step we used (3.40) with $n = 1$.

Combining (3.45) and (3.43) one finds

$$|B_n - B_{n-1}| \leqslant K_2 p |\ln p| (K\sigma^2 |\ln p|)^{n-1} \qquad n \geqslant 2. \tag{3.46}$$

We see that f_n and B_n converge (convergence is governed by a geometric series) if $K\sigma^2|\ln p| < 1$. This condition will be met if, in addition to our previous restrictions, we choose $\alpha < K^{-1}$. Uniform convergence of B_n with respect to $(p, \sigma) \in G_\alpha$ is immediate since $p|\ln p|$ is bounded. In the case of f_n we write the right-hand side of (3.45) as $K_1(\sigma^{(n-1)/2}|\ln p|)(K\sigma^{3/2}|\ln p|)^{n-1}$ and note that now $\sigma^{(n-1)/2}|\ln p| \leqslant 1$ ($n \geqslant 3$). Hence the sequence f_n also converges uniformly in G_α. That the limits f and B satisfy the differential equation (3.4) follows by standard arguments from (3.9) which also holds in the limit. This proves theorem 3.1.

4. Expansion of $E(R)$ and a conjecture

The error estimate

$$|B - B_n| \leqslant \text{constant} \times p |\ln p| (K\sigma^2 \ln p)^n \tag{4.1}$$

is an immediate consequence of (3.46). In particular

$$B=B_1+\mathrm{O}(\sigma^2 p(\ln p)^2). \tag{4.2}$$

Since $\sigma=\mathrm{O}(p^2)$ for the solution of (2.8), the error in (4.2) will translate into an error of $\mathrm{O}(p^5(\ln p)^2)$ in the subsequent expansion for $\sigma(p)$ and this, in turn, will give rise to an error of $\mathrm{O}(R^9(\ln R)^2)$ in the expansion for $E(R)$. The order of this error will be the criterion for truncating the following expansion (4.6) for B_1. Setting $x=4p$, $y=2\sigma$ we have by (3.8) and (3.20)

$$B_1=\left(x\int_x^\infty \mathrm{e}^{-t}t^{y-1}\,\mathrm{d}t\right)\Big/\left(\int_x^\infty \mathrm{e}^{-t}t^{y}\,\mathrm{d}t\right). \tag{4.3}$$

Moreover, we have the following series representations.

$$\begin{aligned}\int_x^\infty \mathrm{e}^{-t}t^{y}\,\mathrm{d}t&=\int_0^\infty \mathrm{e}^{-t}t^{y}\,\mathrm{d}t-x^{y+1}\int_0^1 \mathrm{e}^{-sx}s^{y}\,\mathrm{d}s\\&=\sum_{n,m,k=0}^{\infty} a_{n,m,k}\,x^n y^m (y\ln x)^k\end{aligned} \tag{4.4}$$

$$\begin{aligned}\int_x^\infty \mathrm{e}^{-t}t^{y-1}\,\mathrm{d}t&=\frac{1}{y}\left(-\mathrm{e}^{-x}x^{y}+\int_x^\infty \mathrm{e}^{-t}t^{y}\,\mathrm{d}t\right)\\&=\frac{1}{y}\sum_{n,m,k=0}^{\infty} b_{n,m,k}x^n y^m (y\ln x)^k\end{aligned} \tag{4.5}$$

and

$$B_1=\frac{x}{y}\sum_{n,m,k=0}^{\infty} c_{n,m,k}x^n y^m (y\ln x)^k. \tag{4.6}$$

The first two series expansions are immediate consequences of the fact that the integrals in the middle members of equations (4.4) and (4.5) are analytic at $x=y=0$ and that x^y can be expanded in powers of $y\ln x$. If we set $\tau=y\ln x$ and pretend that x, y and τ are independent complex variables, the series (4.4) and (4.5) converge for $|x|<\infty$, $|y|<1$, $|\tau|<\infty$. We now claim that the series in (4.6) converges for all x, y such that $(p,\sigma)=(x/4, y/2)\in G_\alpha$ when α is sufficiently small. The point to be noted is that $\sup\{|\tau|: (p,\sigma)\in G_\alpha\}=2$ (if $\alpha<(2\ln 2)^{-1}$ so that $4p<1$) and thus does not get smaller with α. But thanks to the extra factor x in $x^{y+1}=x\,\mathrm{e}^{\tau}$, the value of the integral in (4.4) is arbitrarily close to 1 if x and y are sufficiently small. Therefore, the quotient in (4.3) has a convergent expansion in a polydisc $D=\{(x,y,\tau)\in\mathbb{C}^3: |x|<\rho_1, |y|<\rho_2, |\tau|<\rho_3\}$ which contains G_α if α is sufficiently small. Moreover, by Cauchy's inequality,

$$|c_{n,m,k}|\leqslant M/(\rho_1^n\rho_2^m\rho_3^k) \tag{4.7}$$

where $M=\sup_D|(y/x)B_1|$.

We will need the following explicit terms of expansion (4.6) (assuming $x>0$, $y\geqslant 0$):

$$\begin{aligned}B_1=(x/y)[&-y\ln x+yc-x(y\ln x)+(c+1)yx-\tfrac{1}{2}(y\ln x)^2+cy(y\ln x)\\&+(b-c^2)y^2-\tfrac{1}{2}x^2(y\ln x)+(3c+2)xy(y\ln x)+(\tfrac{3}{4}+\tfrac{1}{2}c)x^2y-\tfrac{3}{2}x(y\ln x)^2\\&+(b-2c^2-2c-1)xy^2-\tfrac{1}{6}(y\ln x)^3-\tfrac{1}{6}x^3(y\ln x)+(\tfrac{11}{36}+\tfrac{1}{6}c)x^3y]+R(x,y)\end{aligned} \tag{4.8}$$

where

$$\begin{aligned} c &= \int_0^\infty \ln t \, e^{-t} \, dt = -0.577\,21 \\ b &= \tfrac{1}{2} \int_0^\infty (\ln t)^2 \, e^{-t} \, dt = 0.989\,06. \end{aligned} \tag{4.9}$$

As we mentioned earlier the expansion (4.8) has been truncated according to the prescription that when we assume $y = O(x^2)$ terms in the remainder R become $O(x^5(\ln x)^2)$. Note that a term of order $x^5(\ln x)^3$ appears as $(x/y)(-\frac{1}{6})(y \ln x)^3$ among the explicit terms. The summation indices in the remainder terms must satisfy either

$$n + 2m + 2k > 6 \tag{4.10}$$

or

$$n + 2m + 2k = 6 \qquad \text{and} \qquad k \leqslant 2. \tag{4.11}$$

Moreover,

$$|R(x, y)| \leqslant c[x^5 \ln x + x(y \ln x)^2 + x^3 \ln x (y \ln x) + x \ln x (y \ln x)^3] \tag{4.12}$$

for $(x/4, y/2) \in G_\alpha$ (α sufficiently small). To explain this estimate we write $d = (d_1, d_2, d_3)$ for (n, m, k) and let $\mathbb{D}$ be the set of all triples obeying (4.10) and (4.11). With each $d \in \mathbb{D}$ we associate the three lattice points $d^{(j)}$ $(j = 1, 2, 3)$ where $d_k^{(j)} = d_k$ if $k \neq j$ and $d_k^{(j)} = d_k - 1$ if $k = j$, and we call a triple $d \in \mathbb{D}$ 'minimal' if for some i, $d_i - 1 \geqslant 0$ and $d^{(i)} \notin \mathbb{D}$. The set of all minimal triples will be denoted by $\tilde{\mathbb{D}}$. If $\tilde{d} \in \tilde{\mathbb{D}}$ let $D(\tilde{d}) = \{d \in \mathbb{D}: d_k \geqslant \tilde{d}_k \text{ for } k = 1, 2, 3\}$. Clearly, the union of all the sets $D(\tilde{d})$ equals $\mathbb{D}$. Thus on substituting (4.7) in (4.6) and using the fact that a geometric series is dominated by its lowest-order term we see that

$$\left| \frac{x}{y} \sum_{\mathbb{D}} c_{n,m,k} x^n y^m (y \ln x)^k \right| \leqslant c \sum_{\tilde{\mathbb{D}}} x^{\tilde{d}_1 + 1} y^{\tilde{d}_2 - 1} (y \ln x)^{\tilde{d}_3}. \tag{4.13}$$

The right-hand side in (4.13) consists of 18 summands. However, since B_1 remains bounded as $y \downarrow 0$ (x fixed) $c_{n,0,0} = 0$ for all n, and thus the terms with $\tilde{d} = (\tilde{d}_0, 0, 0)$ can be dropped from (4.13). If we now pick any two of the remaining summands and divide one by the other, it may happen that the ratio goes to zero uniformly in G_α as $\alpha \downarrow 0$. In this sense, for example, the term $x(y \ln x)^2$ ($\tilde{d} = (0, 1, 2)$) dominates the term $x^2 y^{-1} (y \ln x)^3$ ($\tilde{d} = (1, 0, 3)$). Then we can disregard the smaller term in the sum (4.13), and modify the constant c instead. By comparing terms in this manner we can reduce their number to four which gives (4.12).

Note that if we let x and y go to zero such that $y \ln x$ stays bounded away from zero, the last term on the right-hand side in (4.12) is the largest, whereas if we assume $y = O(x^2)$ it is the smallest. The equation (2.8) can also be written as

$$\sigma = C_{\text{inner}}(p) - 2p\sigma - \sigma^2 + \sigma^2 B. \tag{4.14}$$

Recalling that the leading term in $C_{\text{inner}}(p)$ is $\frac{2}{3}p^2$ it follows, by a simple continuity argument, that (4.14) has a solution $\sigma(p) = \frac{2}{3}p^2 + O(p^3)$. This solution is unique because $H(R)$ has a unique eigenvalue converging to -2 as $R \downarrow 0$. This follows from a simple perturbation argument (see § 5). For completeness, we mention that one is not forced to resort to perturbation theory here. Instead, one can show that the right-hand side in (4.14) is analytic as a function of σ in a suitable neighbourhood of zero and then appeal to Rouché's theorem. This argument only applies to solutions that lie in G_α (i.e. a properly modified set G_α if σ is complex) whereas the perturbation argument is more general.

To find the expansion of $E(R)$ we followed BBS (equations (56)–(59)). A HP-67 was used to program some lengthy algebraic expressions for the numerical coefficients. Therefore, we give some of the coefficients in decimal notation, although they are really rational numbers combined with b and c. Choosing the variables $s=2R$ as in BBS the result can be stated in the form

$$E(R)=-2+\sum_{n=2}^{9}\sum_{m=0}^{3}a_{nm}s^n(s^2\ln s)^m+o(s^9(\ln s)^3) \tag{4.15}$$

where the non-vanishing coefficients read

$a_{20}=\frac{2}{3}$	$a_{41}=\frac{2}{9}$	$a_{42}=\frac{2}{27}$
$a_{30}=-\frac{2}{3}$	$a_{60}=-0.288\,69$	$a_{61}=-0.184\,64$
$a_{40}=\frac{22}{135}$	$a_{32}=-\frac{1}{27}$	$a_{86}=-0.134\,29$
$a_{31}=-\frac{2}{9}$	$a_{51}=-0.128\,67$	$a_{33}=-\frac{1}{243}\ (=-\frac{1}{3^5})$
$a_{50}=0.276\,96$	$a_{70}=0.178\,64.$	

Byers Brown and Powers (1970) found that when $E(R)$ is evaluated up to order R^5 the approximation is good for R less than about 0.2. We had originally hoped to see a significant increase or decrease in the 'radius of convergence' if terms up to order $R^9(\ln R)^3$ were included, but the numerical evaluation does not provide enough evidence for either conclusion. The reason for choosing s and $s^2\ln s$ as the basic parameters is the following.

Conjecture. $E(R)$ has the convergent expansion

$$E(R)=-2+\sum_{n,m=0}^{\infty}b_{n,m}R^n(R^2\ln R)^m \tag{4.16}$$

provided R is sufficiently small.

We have been unable to prove this conjecture. However, our attempts to do so have at least convinced us that from among all terms of the form $R^n(\ln R)^m$ only those indicated in (4.16) do actually occur. We can prove this conjecture in two special situations, namely (i) if B is simply replaced by B_1 and (ii) in the Tibbs–Wannier model (Chen 1958, Wannier 1943), i.e. when $V_R(\boldsymbol{x})$ is replaced by its spherical average. In both cases the proof is a direct consequence of the implicit function theorem along with suitable substitutions similar to those made in the appendix to Klaus and Simon (1980).

5. Some comments on the united atom approximation

If the Hamiltonian $H(R)$ is written as

$$H(R)=-\tfrac{1}{2}\Delta-(2/r)+V_R(\boldsymbol{x})\equiv H_c+V_R(\boldsymbol{x}) \qquad (r=|\boldsymbol{x}|) \tag{5.1}$$

where

$$V_R(\boldsymbol{x}) = (2/r) - |\boldsymbol{x} - \tfrac{1}{2}\boldsymbol{R}|^{-1} - |\boldsymbol{x} + \tfrac{1}{2}\boldsymbol{R}|^{-1} \tag{5.2}$$

then owing to the estimate

$$|V_R(\boldsymbol{x})| \leqslant cR^{\epsilon}(r^{-1-\epsilon} + |\boldsymbol{x} - \tfrac{1}{2}\boldsymbol{R}|^{-1-\epsilon} + |x + \tfrac{1}{2}\boldsymbol{R}|^{-1-\epsilon}) \qquad 0 < \epsilon \leqslant 1 \tag{5.3}$$

V_R is a small perturbation of H_c in the sense of relatively bounded operators (respectively in the sense of quadratic forms if $\epsilon \geqslant \frac{1}{2}$). Therefore, $E(R)$ can be expressed as an absolutely convergent series

$$E(R) = \sum_{n=0}^{\infty} E^{(n)} \qquad E^{(0)} = -2 \tag{5.4}$$

where

$$E^{(0)} = -2 \qquad E^{(1)} = (\phi, V_R\phi) \qquad E^{(2)} = -(\phi, V_R S V_R \phi)$$
$$E^{(3)} = (\phi, V_R S V_R S V_R \phi) - (\phi, V_R S^2 V_R \phi)(\phi, V_R \phi) \tag{5.5}$$

etc. are the well known relations from perturbation theory (Kato 1966). Here $\phi = 2^{2/3}\pi^{-1/2}\,\mathrm{e}^{-2r}$ obeys $H_c\phi = -2\phi$ and $S = (H_c + 2)^{-1}(1 - \phi(\phi, \cdot))$ is the reduced resolvent. Closed expressions for $E^{(n)}$ are known only when $n = 1, 2$ (Levine 1974). Expanding them yields

$$-2 + E^{(1)} + E^{(2)} = -2 + \tfrac{2}{3}(2R)^2 - \tfrac{2}{3}(2R)^3 + \tfrac{43}{540}(2R)^4 - \tfrac{1}{9}(2R)^5 \ln R + \mathrm{O}(R^5) \tag{5.6}$$

which agrees with (1.2) up to order R^3. Thus the missing terms in R^4 and $R^5 \ln R$ must be contained in $E^{(n)}$ where $n \geqslant 3$. Of course, one hopes that only $n = 3$ matters and this will indeed be the case. In this connection BBS remark in § E of their paper that it appears to be very difficult to predict the order in R of $E^{(n)}$ for the united atom treatment. Fortunately, one does not need to know the order exactly; it suffices to have an effective estimate, namely

$$|E^{(n)}| \leqslant CR^{n+1} \qquad n \geqslant 1. \tag{5.7}$$

Incidentally, this estimate is sharp for $n = 1, 2, 3$. Inequality (5.7) is a consequence of the estimates

$$\|S^{1/2} V_R \phi\| \leqslant CR^{3/2} \tag{5.8}$$

$$\|S^{1/2} V_R S^{1/2}\| \leqslant CR \tag{5.9}$$

which, since $S^{1/2}(-\Delta + 1)^{1/2}$ is bounded, need only be proved when S is replaced by $(-\Delta + 1)^{-1}$. Then (5.8) follows from

$$\|(-\Delta + 1)^{-1/2} V_R \phi\|^2 = (\phi_R, V_R(-\Delta + 1)^{-1} V_R \phi)$$
$$\leqslant CR^3 \int \frac{V_{\hat{R}}(\boldsymbol{x}) V_{\hat{R}}(\boldsymbol{y})}{|\boldsymbol{x} - \boldsymbol{y}|}\, \mathrm{d}^3x\, \mathrm{d}^3y \qquad \hat{R} = (1, 0, 0) \tag{5.10}$$

where in the last step we used scaling. The integral is finite since $V_R(x) = \mathrm{O}(|x|^{-3})$ at infinity. Inequality (5.9) is a consequence of (5.3) if we put $\varepsilon = 1$. Thus $\Sigma_{n=4}^{\infty} E^{(n)} \leqslant CR^5$ and also $(\phi, V_R S^2 V_R \phi)(\phi, V_R \phi) \leqslant CR^5$, so that the term $R^5 \ln R$ must be contained in the matrix element

$$(\phi, V_R S V_R S V_R \phi). \tag{5.11}$$

To analyse this expression we use the representations for the kernels of S_l where S_l ($l = 0, 1, 2, \ldots$) denotes the projection of S onto the subspace of angular momentum l (Hameka 1968), and we expand V_R in Legendre polynomials. Then we are reduced to study certain explicit one-dimensional integrals. In the process we discovered that it is relatively easy (although still pretty tedious) to track down the terms in $R^5 \ln R$ compared with those in R^4. As a result, we have concentrated on the logarithmic terms and we have found the following contributions:

$$(\phi, V_R S_0 V_R S_0 V_R \phi): -\tfrac{1}{15}(2R)^5 \ln R \tag{5.12}$$

$$\begin{aligned}(\phi, V_R S_0 V_R S_{2m} V_R \phi)&\\ = (\phi, V_R S_{2m} V_R S_0 V_R \phi)&: \frac{4}{3(4m+5)(4m+3)(4m-3)(4m-1)}\\ &\times (2R)^5 \ln R \qquad (m = 1, 2, \ldots).\end{aligned} \tag{5.13}$$

Summing over m and adding (5.12) gives $-\frac{1}{9}(2R)^5 \ln R$ and thus together with (5.6) leads to the same coefficient as in (1.2). In the course of our investigations we also discovered that due to a 'conspiracy between angular momenta' in second order, no terms in $R^4 \ln R$ occur. The only matrix elements containing such terms are $(\phi, VS_0 V\phi)$ and $(\phi, VS_2 V\phi)$ and their respective contributions are $\pm\frac{1}{9}(2R)^4 \ln R$.

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References

Byers Brown W and Powers J D 1970 *Proc. R. Soc.* A **317** 545
Byers Brown W and Steiner E 1966 *J. Chem. Phys.* **44** 3934
Chakravarty S K 1939 *Phil. Mag.* **28** 423
Chen T C 1958 *J. Chem. Phys.* **29** 347
Grosse H, Hertel P and Thirring W 1978 *Acta Phys. Austriaca* **49** 89
Guerrieri B and Hunter C 1982 *Stud. Appl. Math.* **LXVI** 217
Hameka H F 1968 *J. Chem. Phys.* **49** 2009
Hoffmann-Ostenhof T 1980 *J. Phys. A: Math. Gen.* **13** 417
Kato T 1966 *Perturbation theory for linear operators* (New York: Springer)
Klaus M and Simon B 1980 *Ann. Phys., NY* **130** 251
Levine I N 1964 *J. Chem. Phys.* **41** 2044
Lieb E and Simon B 1978 *J. Phys. B: At. Mol. Phys.* L537
Wannier G H 1943 *Phys. Rev.* **64** 358