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Behavior of Molecular Potential Energy Curves for Large Nuclear Separations

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Abstracts

We prove by elementary geometric methods and within the Born–Oppenheimer approximation that as the nuclei of a molecule are dissociated into spatially separated clusters, the discrete molecular energies approach sums of the energies of isolated subsystems. Our methods also show that the spectral projections associated with the discrete molecular spectrum asymptotically approach direct sums of suitable spectral projections for the isolated subsystems. These results apply to any system of particles interacting by asymptotically vanishing pair potentials. We prove that the $1/R$ expansion for discrete molecular potential curves is asymptotic as $R \to \infty$, and we discuss the behavior of the coefficients of the $1/R$ expansion for the ground state of H_2^+.

Nous prouvons par des méthodes géométriques élémentaires et dans le cadre de l'approximation de Born–Oppenheimer, que quand les noyaux d'une molécule sont dissociés en amas séparés dans l'espace, les énergies moléculaires discrètes tendent vers la somme des énergies des sous-systèmes isolés. Nos méthodes montrent aussi que les projections spectrales associées au spectre moléculaire discret tendent asymptotiquement vers des sommes directes de projections spectrales convenables pour les sous-systèmes isolés. Ces résultats s'appliquent à n'importe quel système de particules qui interagissent par des potentiels de paire s'annulant asymptotiquement. Nous prouvons que le développement en $1/R$ pour des courbes de potentiel moléculaires discrètes est asymptotique quand $R \to \infty$, et nous discutons le comportement des coefficients de ce développement pour l'état fondamental de H_2^+.

Wir beweisen durch elementare geometrische Methoden und im Rahmen der Born–Oppenheimer-Näherung, dass, wenn die Kerne eines Moleküls in räumlich separierten Clusters dissoziiert werden, die diskreten Molekülenergien Summen der Energien der isolierten Untersysteme zustreben. Unsere Methoden zeigen auch, dass die mit dem diskreten Molekularspektrum assoziierten Spektralprojektionen asymptotisch direkten Summen von geeigneten Spektralprojektionen für die isolierten Untersysteme zustreben. Diese Ergebnisse sind für irgendein System von Teilchen gültig, die durch asymptotisch verschwindende Paarpotentiale wechselwirken. Wir beweisen, dass die Entwicklung in $1/R$ für diskrete molekulare Potentialkurven wenn $R \to \infty$ asymptotisch ist, und wir diskutieren das Verhalten der Koeffizienten dieser Entwicklung für den Grundzustand von H_2^+.

1. Introduction

In this paper we want to consider a class of problems of which the simplest is the following: Fix a positive integer N. Let Z_A, Z_B be two positive numbers. For

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every $R>0$, let $H(R)$ be the operator

$$H(R)=\sum_{n=1}^{N}(-\Delta_n - Z_A|\mathbf{r}_n|^{-1} - Z_B|\mathbf{r}_n - R\hat{e}|^{-1}) + \sum_{1\le i<j\le N}|\mathbf{r}_i-\mathbf{r}_j|^{-1} \tag{1.1}$$

as an operator on $L^2(\mathbb{R}^{3N})$, where a point in $\mathbb{R}^{3N}$ is $(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ and $\hat{e}$ is a fixed unit vector in $\mathbb{R}^3$. The problem is to show that as $R\to\infty$ the discrete eigenvalues of $H(R)$ approach precisely sums of those of isolated atoms or ions. More generally, we want to prove that the asymptotic vanishing of the potential between two systems implies asymptotic separation of variables for the discrete eigenfunctions, modulo a finite sum to incorporate symmetry.

There are several reasons for our interest in this problem, which is quite transparent physically. In the first place, there are subtleties associated with the fact that some of the eigenvalues of the isolated atoms may lie inside the continuum for another allowed breakup of the system into two ions. Ahlrichs' previous analysis [1] of the $1/R$ expansion is incomplete in his lack of treatment of this question and of the general asymptotic question. Secondly, the only previous rigorous proof of the asymptotic result is by Combes and Seiler [2] (for the case $N=1$, there is an earlier result of Aventini and Seiler [3]); their proof depends on a detailed analysis of Weinberg–van Winter equations for $H(R)$. Such an intuitively simple result should not depend on such elaborate machinery and our goal here is to give a very elementary proof. Indeed, since we choose the kinematics carefully, the proof is a rather effortless application of the min–max principle. Our use of geometric ideas to replace resolvent equations is motivated, in part, by the recent success of such replacements in various problems [4–7].

To state our main results, we need some preliminary notation. We label 2^N ways of breaking $\{1,\ldots,N\}$ into two disjoint sets, $C_0(a)$ and $C_1(a)$, by an index a running from 1 up to 2^N. We let $\delta_i(a)=0$ if $i\in C_0(a)$, $=1$ if $i\in C_1(a)$.

$$H_a=\sum_{n=1}^{N}(-\Delta_n)-\sum_{i\in C_0(a)}Z_A|r_i|^{-1}-\sum_{i\in C_1(a)}Z_B|r_i|^{-1} + \sum_{i<j;\,i,j\in C_0(a)}|r_i-r_j|^{-1}+\sum_{i<j;\,i,j\in C_1(a)}|r_i-r_j|^{-1}. \tag{1.2}$$

Finally, we take a new Hilbert space

$$\mathscr{H}_\infty=\bigoplus_{a=1}^{2N}L^2(\mathbb{R}^{3N}),$$

and let

$$H_\infty=\bigoplus_{a=1}^{2N}H_a.$$

Intuitively, as $R\to\infty$, the electrons in bound states must choose one or the other nucleus to stay near and the resulting 2^N choices are labeled by a. For $R\to\infty$, the possible electronic configurations are thus better handled by $\mathscr{H}_\infty$ than in a single $L^2(\mathbb{R}^{3N})$.

Finally, we recall that given any operator A which is bounded from below with spectral projections $E_I(A)$, one defines

$$\mu_k(A)=\inf\{C\,|\,\dim E_{(-\infty,C]}(A)\ge k\}.$$

Then clearly $\mu_\infty=\lim_{k\to\infty}\mu_k$ is the bottom of the essential spectrum and either (a) $\mu_k<\mu_\infty$, in which case μ_k is the kth eigenvalue (counting multiplicity) from the bottom, or (b) $\mu_k=\mu_\infty$, in which case there are at most $k-1$ eigenvalues (counting multiplicity) in $(-\infty,\mu_\infty)$. Moreover [8], μ_k is given by the min–max principle

$$\mu_k(A)=\max_{\psi_1,\ldots,\psi_{k-1}}[\min_{\phi}\{(\phi,A\phi)\,|\,\|\phi\|=1,\ \phi\in Q(A),\ \phi\perp\psi_i\}].$$

Our main result proven in Sec. 2 is

Theorem 1.1.

$$\lim_{R\to\infty}\mu_k(H(R))=\mu_k(H_\infty)$$

for all k including $k=\infty$.

Note that to list $\mu_k(H_\infty)$, one need only list all the $\mu_k(H_a)$ and then combine them into one list. As it stands, Theorem 1.1 is of only limited interest for $N>2$, since in this case the continuum on the physical subspace (that obeying the Pauli principle) typically lies above the continuum with no symmetry and Theorem 1.1 only deals with eigenvalues below the continuum. To state a version of Theorem 1.1 with symmetry we first single out:

Definition. By an *allowed symmetry* we mean a linear map S which is a product of (a) rotations about an axis running from $\bar{0}$ to $\hat{e}$; (b) reflections in planes containing $\bar{0}$ and $\hat{e}$; (c) permutations of the electrons; in case $Z_A=Z_B$, rotations or reflections interchanging $R\hat{e}$ and 0. By $U(S)$ we mean the unitary map on $L^2(\mathbb{R}^{3N})$, which realizes the symmetry. By $U_\infty(S)$ we mean the obvious map on $\mathscr{H}_a$; explicitly: In cases (a) and (b), $U_\infty(S)$ leaves each $L^2(\mathbb{R}^{3N})$ set-wise invariant and operates in the obvious coordinate-wise way on each factor. In case (c), for fixed a, we write $S=S_1S_2$, where S_2 interchanges particles in a given $C_i(a)$ and S_1 interchanges particles between clusters. Then on the ath factor $U(S)=U(S_1)U(S_2)$, where $U(S_2)$ leaves the ath factor in $\mathscr{H}_\infty$ set-wise fixed and acts in the obvious coordinate way, and $U(S_1)$ takes the ath factor into the bth factor with $C_i(b)=S_1[C_i(a)]$ and acts in the obvious way. In case (d), where S is reflection in the plane $\{x\,|\,x\cdot\hat{e}=R/2\}$, $U_\infty(S)$ acts by taking the ath factor into the bth factor with $C_i(b)=C_{1-i}(a)$ and by interchanging coordinates and reflecting in the plane $\{x\,|\,x\cdot\hat{e}=0\}$. Any S of type (d) can be written $S=S_1S_2$ with S_2 of type (b) and S_1 the above reflection. We take $U(S)=U(S_1)U(S_2)$.

In Sec. 2 we also prove

Theorem 1.2. Fix a subgroup K of allowed symmetries and an irreducible representation W of K. Let $\mathscr{H}_W=\{\psi\in L^2(\mathbb{R}^{3N})$ so that ψ transforms under $W\}$

and $H^{(W)}(R) = H(R)\mathscr{H}_W$. Define $\mathscr{H}_{W,\infty}$ and $H_\infty^{(W)}$ similarly. Then, we have

$$\lim_{R\to\infty} \mu_k(H^{(W)}(R)) = \mu_k(H_\infty^{(W)})$$

for all k including $k = \infty$.

Remarks. (i) ψ transforms under W, means that

$$\psi = \sum_{i=1}^{N} a_i\phi_i, \quad N = \dim(W)$$

and

$$[U(S)\phi_i] = \sum_{j=1}^{N} W_{ji}(S)\phi_j$$

for all $S \in K$.

(ii) If K contains symmetries of type (d), then $U(S)$ and hence $\mathscr{H}_W$ are R-dependent and should really be written $U_R(S)$ and $\mathscr{H}_{R,W}$.

(iii) For example, we can take K to be the group of permutations and W the totally antisymmetric space or W can be one of the other representations allowed by the Pauli principle (Young's tableaux with at most two columns).

(iv) For the case of many nuclei, the symmetries of type (a), (b) are those which leave all nuclei fixed and those of type (d) permute nuclei of identical charges.

We want to indicate certain extensions of these theorems that one can make with little effort:

(i) One can allow many nuclei at $R_1, \ldots, R_n$ in l clusters, $Q_1, \ldots, Q_l$. Fix l distinct vectors $V_1, \ldots, V_l$ and for each R, let $H(R)$ be the Hamiltonian where the ith nucleus is at $R_i + RV_{\Delta(i)}$ with $\Delta(i)$ equal to the cluster number of i. Then a has to run through l^N indices. Otherwise the proof given in (ii) extends with no real change.

(ii) The proofs in Sec. 2 extend with no real effort to general local potentials V_{ij} ($i = A$ or B allowed) obeying

$$(\phi, |V_{ij}|\phi) \le a(R)(\phi, (H_0+1)\phi) \tag{1.3}$$

for all $\phi \in S_R$ with $a(R) \to 0$ as $R \to \infty$. In (1.3), $H_0 = (-\Delta)$, and

$$S_R = \{\phi \in L(\mathbb{R}^3) | \operatorname{supp} \phi \in \{x | |x| > R\}\}$$

and obeying

$$V_{ij} \ge 0 \text{ and local; all } i, j \text{ both electron coordinates.} \tag{1.4}$$

(iii) By an extra argument indicated at the end of Sec. 2, one can eliminate condition (1.4).

(iv) One can also accommodate nonlocal potentials with extra argument.

We note that the Combes–Seiler proof [2] accommodates (i). It also accommodates (ii) under the hypothesis that V_{ij} is H_0 compact; this is somewhat stronger than (1.3). (Combes and Seiler begin their paper by saying they assume all

potentials are dilation analytic and this hypothesis is used in some of their other results, but their proof of the analog of Theorem 1.1 does not use dilation analyticity.) Finally, Combes and Seiler do not discuss the theorem with symmetry but it should be possible to do so with their methods since the Weinberg–van Winter equations combine nicely with a symmetry analysis [5, 9, 10].

We can now explain our criticism of the Ahlrichs paper [1]. Let λ_0 be a discrete eigenvalue of some H_a which lies above $\mu_\infty(H_\infty) = \inf_a \mu_\infty(H_a)$. For example, take $Z_A = 2$, $Z_B = 1$, and $N = 2$. For the a with both electrons in C_1, there is a bound state formed, the ground state of H^- at energy $\lambda_0 = -14.3$ eV. The continuum begins at the binding energy of $He^+ = -54.4$ eV.

For any finite R, one expects the eigenvalue λ_0 to dissolve into continuum; i.e., a process like $H^- + He^{2+} \to H^+ + He^+ + e^-$ occurs. There is, therefore, an important difference between eigenvalues below $\mu_\infty(H_\infty)$ which are stable (this is precisely what is proven in Theorems 1.1 and 1.2) and those above $\mu_\infty(H_\infty)$. Ahlrichs implicitly assumes that for every eigenvalue of H_∞, there are eigenvalues of $H(R)$ nearby. We prove this for discrete eigenvalues and, given this proof, the Ahlrichs paper is basically correct (at least for eigenvalues which are nondegenerate after complete symmetry reduction). Nevertheless, it seems to us that it is worth rearranging the argument to avoid certain difficulties in the Ahlrichs method; we do this in Sec. 3. For the case $\lambda_0 > \mu_\infty$, the Ahlrichs method establishes the existence of what is called a pseudoeigenvalue (see Section XII.5 of Ref. 8) and as a result the existence of spectral concentration in a suitable sense. We would presume much more is true; namely, there should be a resonance $E(R)$, in the sense of exterior complex scaling [11, 12] for all large enough R, with $E(R) \to \lambda_0$ as $R \to \infty$ and $\Gamma(R) = -2 \operatorname{Im} E(R) = O(R^{-n})$ for all n. Because of the singularities in exterior scaling as $R \to \infty$, this is probably difficult to prove.

In Sec. 4, we consider the coefficients of the $1/R$ expansion for H_2^+. In many ways H_2^+ can be interpreted as a double-well problem. For by using scaling, $H(R)$ is unitarily equivalent to

$$R^{-2}(-\Delta + R|x|^{-1} + R|x - \hat{e}|^{-1}),$$

which is clearly a double-well problem, somewhat analogous to the double-well oscillator

$$p^2 + x^2 + 2\lambda x^3 + \lambda^2 x^4.$$

For the double-welled oscillator, it has been determined numerically (and within the formal application of Euler's method in path space) [13] that the Rayleigh–Schrödinger coefficients diverge as $n!$ (with an asymptotically constant sign). Our analysis in Sec. 4 suggests that the same is true for H_2^+. In addition, the doubling of eigenvalues that occurs due to exchange (in our language, there are two H_a's each unitarily equivalent and so two eigenvalues approaching each one of H_a) is like the doubling which takes place for the double-welled oscillator [8]. The theory which Harrell developed [14, 15] to obtain rigorously the asymptotics of the size of the splitting of the double-well levels works also to control rigorously the asymptotics of the exchange splitting in H_2^+ thereby making rigorous earlier results of Damburg and Propin [16].

2. Basic Theorems

Here we prove Theorems 1.1 and 1.2. The basic idea will be to use eigenfunctions for H_∞ as variational functions for $H(R)$ to show that

$$\mu_k(H(R)) \le \mu_k(H_\infty) + O(R^{-1}) \tag{2.1}$$

and eigenfunctions of $H(R)$ as trial functions for H_∞ to show that

$$\mu_k(H_\infty) \le \mu_k(H(R)) + O(R^{-1}). \tag{2.2}$$

[We only prove (2.1), (2.2) when $\mu_k(H_\infty) < \mu_\infty(H_\infty)$. If $\mu_k(H_\infty) = \mu_\infty(H_\infty)$, then we do not know that the error is $O(R^{-1})$, only $o(1)$.]

To prove (2.1), we define a map $I_R : \mathscr{H}_\infty \to \mathscr{H} \equiv L^2(\mathbb{R}^{3N})$ by

$$I_R(\psi)(r_i) = \sum_a \psi_a(r_i + \delta_a(i)R\hat{e}).$$

Thus, I_R puts the ψ_a component in the proper region of configuration space. For later purposes we note that for any allowed symmetry

$$U(S)I_R = I_R U_\infty(S). \tag{2.3}$$

Lemma 2.1. For any fixed $\phi, \psi \in \mathscr{H}_\infty$,

$$\lim_{R\to\infty} (I_R\phi, I_R\psi) = (\phi, \psi). \tag{2.4}$$

If moreover $\phi, \psi \in Q(H_\infty)$, the form domain of H_∞, then

$$\lim_{R\to\infty} (I_R\phi, H(R)I_R\psi) = (\phi, H_\infty\psi). \tag{2.5}$$

If moreover, $\|e^{\alpha|x|}\phi\|$, $\|e^{\alpha|x|}\psi\|$, $\|e^{\alpha|x|}|H_\infty|^{1/2}\phi\|$, $\|e^{\alpha x}|H_\infty|^{1/2}\psi\|$ are all bounded for some $\alpha > 0$, then the error in the limit in (2.4) is $O(e^{-\delta|R|})$ for suitable $\delta > 0$ and in (2.5) is $O(R^{-1})$.

Proof. For (2.4), we need only show that for $a \ne b$, we have

$$\lim_{R\to\infty} \int \overline{\phi_a(r_i + \delta_a(i)R\hat{e})}\ \psi_b(r_i + \delta_b(i)R\hat{e})\, d^{3N}r_i = 0$$

and is $O(e^{-\delta|R|})$ when $\|e^{\alpha|x|}\phi_a\|_2 < \infty$, $\|e^{\alpha|x|}\psi_b\| < \infty$. This is obvious.

For (2.5), we let $D = I_R^* H(R) I_R - H_\infty$ and let D_{ab} be the matrix components of D in $\mathscr{H}_\infty = \bigoplus_a L^2$. Then, for $a \ne b$, we have

$$(\phi_a, D_{ab}\psi_b) \to 0$$

[respectively, $O(e^{-\delta|R|})$ as in the above argument]. For $a = b$, we have

$$(\phi_a, D_{aa}\psi_a) = \int \overline{\phi_a(r_i + \delta_a(i)R\hat{e})}\quad W_a(r_i, R)\psi_a(r_i + \delta_a(i)R\hat{e})\, d^{3N}r,$$

with

$$W_a(r_i, R) = -\sum_{i\in C_0(a)} Z_B|r_i - R\hat{e}|^{-1} - \sum_{i\in C_1(a)} Z_A|r_i|^{-1} + \sum_{i\in C_0, j\in C_1} |r_i - r_j|^{-1}.$$

Using the fact that $\nabla\psi \in L^2$ to control the local singularities of W_a one easily sees that $(\phi_a, D_{aa}\psi_a)$ goes to zero [respectively, $O(R^{-1})$]. ∎

Theorem 2.2. If $\mu_k(H_\infty) < \mu_\infty(H_\infty)$, then (2.1) holds. If $\mu_k(H_\infty) = \mu_k(H_a)$, then (for $k < \infty$)

$$\mu_k(H(R)) \le \mu_k(H_\infty) + o(1). \tag{2.1'}$$

Proof. If $\mu_k(H_\infty) < \mu_\infty(H_\infty)$, then we can find $\eta_1, \dots, \eta_k$, eigenvectors of H_a with $H_\infty\eta_i = E_i\eta_i$, $E_i \le \mu_k(H_\infty)$. Then the η_i's have exponential falloff (see Sec. XIII.11 of Ref. 8).

Let V be the span of the η's. Then

$$\mu_k(H(R)) \le \sup\{(I_R\eta, H(R)I_R\eta)/(I_R\eta, I_R\eta) \mid \eta \in V, \|\eta\| = 1\}.$$

This quotient is $(\eta, H_\infty\eta) + O(R^{-1})$ by Lemma 2.1 and by compactness of the sphere, the $O(R^{-1})$ error is uniform in η for fixed k (essentially we need only look at convergence of finitely many matrix elements). This proves (2.1).

If $\mu_k(H_\infty) = \mu_\infty(H_\infty)$, then given ε, we can find $\eta_1, \dots, \eta_k$ orthonormal in $E_{(-\infty, \mu_k(H_\infty)+\varepsilon)}(H_\infty)$ and proceed as above to see that

$$\varlimsup_{R\to\infty} \mu_k(H(R)) \le \mu_k(H_\infty) + \varepsilon.$$

Since ε is arbitrary, (2.1) holds. ∎

For the opposite direction, we use an idea from Ref. 17; namely, let $\{J_\alpha\}_{\alpha\in I}$ be a family of real-valued functions with

$$\sum_\alpha J_\alpha^2 = 1 \quad\text{and}\quad \sum_\alpha |\nabla J_\alpha|^2 < \infty.$$

Then, we have

$$\sum_\alpha \|\nabla J_\alpha\phi\|^2 = \sum_\alpha \{(\nabla\phi, J_\alpha^2\nabla\phi) + [\phi, (\nabla J_\alpha)^2\phi] + (\nabla\phi, J_\alpha\nabla J_\alpha\phi) + (J_\alpha\nabla J_\alpha\phi, \nabla\phi)\}$$

$$= \|\nabla\phi\|^2 + \left\|\left[\sum_\alpha (\nabla J_\alpha)^2\right]^{1/2}\phi\right\|, \tag{2.6}$$

since

$$\sum_\alpha J_\alpha\nabla J_\alpha = \tfrac{1}{2}\nabla\Big(\sum_\alpha J_\alpha^2\Big) = 0.$$

Define a function θ on R^3 by

$$\theta(x) = \begin{cases} 0, & \text{if } x\cdot\hat{e} > \frac{2}{3}, \\ \frac{1}{2}\pi(-3\hat{x}\cdot\hat{e} + 2), & \text{if } \frac{1}{3} \le x\cdot\hat{e} \le \frac{2}{3}, \\ \frac{1}{2}\pi, & \text{if } x\cdot\hat{e} < \frac{1}{3}. \end{cases}$$

Let $\eta_0(x) = \cos[\theta(x)]$, $\eta_1(x) = \sin[\theta(x)]$, and let

$$J_{a,R}(r_i) = \prod_{i=1}^{N} \eta_{\delta_a(i)} \frac{x}{R}.$$

Thus $J_{a,R}$ is unity precisely in the region where the electrons are in the clusters appropriate to a. Note that

$$\sum_a J_{a,R}^2 = 1, \tag{2.7}$$

$$\sum_a \|(\nabla J_a)^2\|_\infty = cR^{-2}. \tag{2.8}$$

Let $J_R : \mathcal{H} \to \mathcal{H}_\infty$ by $(J_R\phi)_a(r_i) = (J_{a,R}\phi)(r_i - \delta_a(i)R)$. By (2.7), we get

$$\|J_R\phi\| = \|\phi\|. \tag{2.9}$$

Moreover, we note that for any allowed symmetry

$$U_\infty(S)J_R = J_R U(S). \tag{2.10}$$

Lemma 2.3. For any $\phi \in Q(H(R))$ and $R \geq 1$:

$$(J_R\phi, H_\infty J_R\phi) \leq (\phi, H(R)\phi) + dR^{-1}\|\phi\|^2, \tag{2.11}$$

where d is a universal constant.

Proof. By (2.6), the only terms in $H(R) - J_R^* H_\infty J_R$ are

(a) $\sum_a (\nabla J_a)^2$,

(b) $\sum_a J_{a,R}^2 \Big(\sum_{i \in C_0(a), j \in C_1(a)} |r_i - r_j|^{-1} \Big)$,

(c) $-\sum_a J_{a,R}^2 \Big(\sum_{i \in C_0(a)} Z_B |r_i - R\hat{e}|^{-1} + \sum_{i \in C_1(a)} Z_A |r_i|^{-1} \Big)$.

By Eq. (2.8), the first term is an operator which is $O(R^{-2})$ and the operator norm of the third term is clearly $O(R^{-1})$. Since the second term is a positive operator, the inequality in (2.11) follows. ∎

Theorem 2.4. Suppose that $\lim_{R\to\infty} \mu_\infty(H(R)) = \mu_\infty(H_\infty)$ and $\mu_k(H_\infty) < \mu_\infty(H_\infty)$. Then (2.2) holds. In any event, for $k < \infty$, we get

$$\mu_k(H_\infty) \leq \mu_k(H(R)) + o(1). \tag{2.2'}$$

Proof. Under the hypotheses of the first sentence we know, by (2.1), that $\mu_k(H(R)) < \mu_\infty(H(R))$ for R large. Thus, we can find a subspace V of dim k with $(\phi, H(R)\phi) \leq \mu_k(H(R))\|\phi\|^2$ for all $\phi \in V$. Then by (2.11) and (2.9), we get

$$(J_R\phi, H_\infty J_R\phi) \leq [\mu_k(H(R)) + dR^{-1}](J_R\phi, J_R\phi)$$

for all $\phi \in V$. Thus, (2.2) holds.

In the general case, we only know that $(\phi, H(R)\phi) \leq (\mu_k(H(R)) + \varepsilon)\|\phi\|^2$, so one only gets (2.2′). ∎

Proof of Theorem 1.1. The result for $k < \infty$ follows from Theorems 2.2 and 2.4. To get the $k = \infty$ result, we use the HVZ Theorem (see Sec. XIII.5 of Ref. 8) which asserts in this case that $\mu_\infty(H(R)) = \mu_1(\tilde{H}(R))$, $\mu_\infty(H_a) = \mu_1(\tilde{H}_\infty)$, where $\tilde{H}(R)$, $\tilde{H}_\infty$ is obtained by considering $N-1$ electrons in place of N. ∎

Remark. We have been careful to keep track of the errors to see that if $\mu_k(H_\infty) < \mu_\infty(H_\infty)$, then $(\mu_k(H(R)) - \mu_k(H_\infty)) = O(R^{-1})$. [In applying Theorem 2.4 we note that by induction on N, $\mu_\infty(H(R)) \to \mu_\infty(H_\infty)$.] Of course, one can say much more; see Sec. 3.

Proof of Theorem 1.2. By (2.3) and (2.10), the maps I_R and J_R take $\mathcal{H}_{W,\infty}$ (respectively, $\mathcal{H}_W$) into $\mathcal{H}_W$ (respectively, $\mathcal{H}_{W,\infty}$) and thus for $k < \infty$, the proof is identical to that above. For $k = \infty$, we need the version of the HVZ theorem with symmetry [9, 10, 5], which implies that

$$\mu_\infty(H^{(W)}) = \min_i \mu_1(\tilde{H}^{(W_i)})$$

for an explicit finite set of W_i's determined by W. ∎

This completes the main part of this section. We now wish to describe how to modify the arguments to accommodate somewhere negative potentials between the "electrons." We emphasize that the rest of this section is unnecessary for treating the molecular case. Therefore we shall only sketch the details.

(i) Instead of breaking $\mathbb{R}^3$ into two regions, $x \circ \hat{e} \in (-\infty, \frac{2}{3}R)$, $x \circ \hat{e} \in (\frac{1}{3}R, \infty)$, we break it into $N+1$ regions:

$$x \circ \hat{e} \in \Big(-\infty, \frac{2R}{3N}\Big), \Big(\frac{R}{3N}, \frac{5R}{3N}\Big), \Big(\frac{4R}{3N}, \frac{8R}{3N}\Big), \ldots, \Big(\frac{(3N-2)R}{N}, \infty\Big)$$

and let a run through $(N+1)^N$ indices rather than through 2^N indices.

(ii) If a corresponds to a decomposition with all electrons in one end or the other, we take $H_a^{(R)}$ as in the general case, independent of R. If a is a different decomposition (we call all such a's, $\mathcal{D}$), we take an R-dependent operator as follows: For each a at least one of the $N+1$ regions has no electrons, so choose $j(a)$ so that

$$\Big(\frac{(3j-1)R}{3N}, \frac{(3j+1)R}{3N}\Big)$$

has no electrons; and let $b(a)$ be the decomposition with all electrons to the left of jr/N lumped to region 0 and all electrons to the right lumped to region N. Let $H_a^{(R)} = J_{a,R} H_{b(a)} J_{a,R}$, where $J_{a,R}$ is picked as in the general proof so that $J_{a,R}$ forces the electrons into the regions specified by a and $\sum_a J_{a,R}^2 = 1$.

(iii) Note that if $a \in \mathcal{D}$

$$\lim_{R\to\infty} \mu_1(J_a H_{b(a)} J_a) \geq \mu_\infty(H_{b(a)}),$$

since at least one electron in $J_a H_{b(a)} J_a$ does not interact with either nucleus so that by the HVZ theorem $\mu_1(J_a H_{b(a)} J_a) \geq \mu_\infty(H_{b(a)}) + o(1)$.

(iv) Thus, for any fixed k if

$$\mu_k\Big(\bigoplus_{a\notin\mathcal{D}} H_a\Big) \le \mu_\infty\Big(\bigoplus_{a\notin\mathcal{D}} H_a\Big),$$

then

$$\mu_k\Big(\bigoplus_{a} H_a\Big) = \mu_k\Big(\bigoplus_{a\notin\mathcal{D}} H_a\Big)$$

for R large.

(v) Since the electrons to the left of $j(a)R/N$, and those to the right of $j(a)R/N$ are at least $2R/3N$ from each other, $H_{b(a)}$ and $H(R)$ only differ by terms which involve interactions between different electrons and therefore for $\phi \in Q(H(R))$,

$$(J_R\phi, H_\infty^{(R)} J_R\phi) = (\phi, H(R)\phi) + O(R^{-1}).$$

(vi) The steps above replace those in the proof of Theorem 2.4 when there may be somewhere negative potentials between "electrons." The arguments leading to Theorem 2.2 go through without change.

3. 1/R Expansion

Here we consider the situation where H_∞ has a discrete nondegenerate eigenvalue or more properly, since H_∞ has few nondegenerate eigenvalues on account of symmetry, where some $H_\infty^{(W)}$ has discrete eigenvalues E_∞ of degeneracy $n = \dim W$ ($H_\infty^{(W)}$ is always a direct sum of n unitarily equivalently operators A^W; thus we mean that A^W has a nondegenerate eigenvalue—henceforth we say "$H_\infty^{(W)}$ has a 'nondegenerate' eigenvalue" to describe this). In this case, Theorem 1.2 tells us that $H^{(W)}(R)$ has a unique eigenvalue $E(R)$ which converges to E_∞ as $R \to \infty$. We will recover the result of Ahlrichs [1] that $E(R)$ has an asymptotic series

$$E(R) \sim \sum_{k=0}^{\infty} a_k R^{-k} \tag{3.1}$$

{i.e., for each m, $R^m[E(R) - \sum_{k=0}^{m} a_k R^{-k}] \to 0$ as $R \to \infty$}. Our method can also be used to establish a norm asymptotic series for a vector $\psi(R)$ in $\mathcal{H}_\infty$ so that $I_R\psi(R)$ is an eigenvector of $H^{(W)}(R)$ with eigenvalue $E(R)$ (I_R is described in Sec. 2). This is also a result of Ahlrichs [1]. Ahlrichs does not anywhere explicitly state that he is assuming nondegeneracy of eigenvalues, but his proofs exploit formal Rayleigh–Schrödinger (RS) series. For the case of C^∞ but nonanalytic perturbations, there is not always a good RS theory, for there are examples where the eigenvectors are not continuous although the eigenvalues are C^∞. Consider the following example of Rellich [18, 29] for simplicity:

$$H(\lambda) = -\exp(-\lambda^{-2})\begin{pmatrix}\cos(2/\lambda) & \sin(2/\lambda)\\ \sin(2/\lambda) & -\cos(2/\lambda)\end{pmatrix},$$

for real $\lambda \ne 0$, $H(0) = 0$. The eigenvalues are

$$E_\pm(\lambda) = \pm e^{-1/\lambda^2},$$

with eigenvectors

$$\phi_+(\lambda) = \begin{pmatrix}\sin(1/\lambda)\\ -\cos(1/\lambda)\end{pmatrix}, \quad \phi_-(\lambda) = \begin{pmatrix}\cos(1/\lambda)\\ \sin(1/\lambda)\end{pmatrix},$$

respectively. $E_\pm$ are C^∞ but $\phi_\pm$ do not have limits as $\lambda \to 0$.

However, there is a well-defined procedure which one can try where if the degeneracy is reduced at finite order, one obtains asymptotic series. We also strengthen a result of Ahlrichs in that we prove that exchange terms are $O(e^{-\delta R})$ rather than just $O(R^{-N})$.

Our proof differs from that of Ahlrichs in two ways:

(i) Ahlrichs first makes a multipole expansion of the potential and then applies perturbation theory. We do things in the opposite order which is technically somewhat simple.

(ii) We control errors by the method of writing $E(R)$ in terms of integrals of resolvents and then the perturbation expansion is just a geometric expansion. The error is then very simple to write down. This method works for virtually all rigorous perturbation problems [8].

Nevertheless, we emphasize that the Ahlrichs proof is similar in spirit to ours; moreover, unlike ours, it works to prove spectral concentration (in a suitable sense) for eigenvalues of H_∞ which are above the continuum limit.

Lemma 3.1. Let E_∞ be a "nondegenerate" discrete eigenvalue of $H_\infty^{(W)}$, and let η_∞ be the corresponding eigenvector. Let $\eta(R)$ be the corresponding eigenvector of $H(R)$. Then [after changing the phase of $\eta(R)$ if necessary], we have

$$\|I_R\eta_\infty - \eta(R)\| \to 0. \tag{3.2}$$

Let η'_∞ be a single nonzero component of η_∞ (component in the direct sum over a sense). Then, we have

$$(I_R\eta'_\infty, \eta(R)) \to (\eta'_\infty, \eta_\infty) \ne 0. \tag{3.3}$$

Proof. Equation (3.3) follows from (3.2) and (2.4). To prove (3.2) we note that by the same method as used in Lemma 2.1, $\|(H(R)I_R - I_R H_\infty)\eta_\infty\| = O(R^{-1})$. Thus since $E(R) \to E_\infty$, $\|(H(R) - E(R))I_R\eta_\infty\| \to 0$. Let

$$d(R) = \operatorname{dist}[E(R), \{\lambda \mid \lambda \in \sigma(H(R))\backslash\{E(R)\}\}]$$

and let $P(R)$ be the projection onto $\eta(R)$. Then

$$\|(1 - P(R))I_R\eta_\infty\| \le d(R)^{-1}\|(H(R) - E(R))I_R\eta_\infty\| \to 0.$$

Since $\|I_R\eta_\infty\| \to \|\eta_\infty\|$ by (2.4), we have proven (3.2). ∎

Let us suppose temporarily that the following holds:

$$E_\infty < \mu_\infty(H_\infty) \tag{3.4}$$

rather than just $E_\infty < \mu_\infty(H_\infty^{(W)})$. This will allow us to talk about $[H(R)-E]^{-1}$ without restricting to symmetry subspaces. At the conclusion of the section, we will discuss what to do when (3.4) fails.

The following result is only needed to show that exchange terms are $O(e^{-\delta R})$. If we were willing to settle for $O(R^{-N})$, then it could be dispensed with.

Lemma 3.2. Fix $\varepsilon>0$ small and $a\in\mathbb{R}^{3N}$. Then for some $\delta>0$, and some $C<\infty$, we have

$$\sup_{|E-E_\infty|=\varepsilon} \|e^{\delta a\cdot x}[H(R)-E]^{-1}e^{-\delta a\cdot x}\|\le C \tag{3.5}$$

for all R sufficiently large.

Proof. We use ideas of Combes and Thomas [19] to find that

$$e^{\delta a\cdot x}(H(R))e^{-\delta a\cdot x}=H_\delta(R),$$

where $H_\delta(R)=H(R)+\delta C_1+\delta^2C_2$, where C_1, C_2 are R-independent operators, C_2 is a constant, and C_1 is $-\Delta$ bounded with relative bound zero. We can thus pick δ so small and R so large that

$$\sup_{\substack{R>R_0\\ |E-E_\infty|=\varepsilon}} [\|\delta C_1[H(R)-E]^{-1}\|+\delta^2\|C_2[H(R)-E]^{-1}\|]\le\tfrac{1}{2}.$$

Therefore, by standard arguments, we get

$$\|[H_\delta(R)-E]^{-1}\|\le 2\|[H(R)-E]^{-1}\|,$$

proving (3.5). ∎

Let

$$\tilde{P}(R)=(2\pi i)^{-1}\oint_{|E-E(R)|=\varepsilon}[E-H(R)]^{-1}\,dE.$$

$\tilde{P}(R)$ differs from $P(R)$, the projection onto $E(R)$, in that we are not projecting onto a symmetry subspace. Typically, there are several different symmetry subspaces $W=W_1,\ldots,W_l$ so that E_∞ is a nondegenerate eigenvalue of $H_\infty^{(W_1)},\ldots,H_\infty^{(W_l)}$, and generally different eigenvalues $E(R)=E_1(R),\ldots,E_l(R)$ each converging to E_∞. $\tilde{P}(R)$ is then the projection onto eigenvectors for any $E_i(R)$. The following result will imply that exchange terms are exponentially small.

Lemma 3.3. Let η_1, η_2 lie in distinct components of $\mathscr{H}_\infty$, and suppose that (3.4) holds. Suppose that $e^{\alpha|x|}\eta_i\in L^2$. Then for some $\delta>0$,

$$(I_R\eta_1,\tilde{P}(R)I_R\eta_2)=O(e^{-\delta R}). \tag{3.6}$$

If, moreover, $\eta_1\in D(H_\infty)$ and $e^{\alpha|x|}H_\infty\eta_1\in L^2$, then

$$(H(R)I_R\eta_1,\tilde{P}(R)I_R\eta_2)=O(e^{-\delta R}). \tag{3.7}$$

Proof. Let $\hat{e}$ be the vector in $\mathbb{R}^3$ defined in (1.1). Given a decomposition a, let δ_a be the vector in $\mathbb{R}^{3N}$ whose ith component is $\delta_a(i)\hat{e}$. Let η_1 (respectively, η_2) be in $\mathscr{H}_a$ (respectively, $\mathscr{H}_b$). Since by hypothesis $a\ne b$, we can find $v\in\mathbb{R}^{3N}$ so that $v\cdot(\delta_b-\delta_a)=1$. By hypothesis and Lemma 3.2,

$$\tilde{\eta}_1=e^{\delta v\cdot(r-\delta_a R)}I_R\eta_1 \quad\text{and}\quad e^{\delta v\cdot(r-\delta_b R)}\tilde{P}(R)I_R\eta_2=\tilde{\eta}_2$$

are in L^2 for some $\delta>0$ with norms uniformly bounded as $R\to\infty$. Thus,

$$(I_R\eta_1,\tilde{P}(R)I_R\eta_2)=e^{-\delta R}(\tilde{\eta}_1,\tilde{\eta}_2)$$

is $O(e^{-\delta R})$, proving (3.6). The proof of (3.7) is similar. ∎

Theorem 3.4. Suppose that (3.4) holds. Let W_1, W_2 be two symmetry types so that E_∞ is a "nondegenerate" eigenvalue of $H_\infty^{(W_i)}$. Let η_i $(i=1,2)$ be the corresponding eigenvectors and suppose that $(\eta_1)_a=c(\eta_2)_a$ for some nonzero constant c and some decomposition a. Then

$$E_1(R)-E_2(R)=O(e^{-\delta R}) \tag{3.8}$$

for some $\delta>0$.

Proof. By (3.3), for R sufficiently large:

$$E_1(R)=(H(R)I_R(\eta_1)_a,\tilde{P}(R)I_R\eta_1)/(I_R(\eta_1)_a,\tilde{P}(R)I_R\eta_1).$$

By Lemma 3.3, all inner products from components $(\eta_1)_b$ with $b\ne a$ are $O(e^{-\delta R})$. Thus,

$$E_1(R)=(H(R)I_R(\eta_1)_a,\tilde{P}(R)I_R(\eta_1)_a)/(I_R(\eta_1)_a,\tilde{P}(R)I_R(\eta_1)_a)+O(e^{-\delta R}). \tag{3.9}$$

This proves (3.8). ∎

Example. Let $N=1$ and suppose we have an eigenvalue E_∞ corresponding to the decomposition $a=\{1\}$. Then by symmetry $b=\{2\}$ is also a decomposition with eigenvalue E_∞. If η_a, η_b are the corresponding eigenvectors related under interchange of electrons, then $(\eta_a\pm\eta_b)/\sqrt{2}=\eta_\pm$ are eigenvectors with different symmetries. By (3.8), the error (i.e., exchange) between the eigenvalues is $O(e^{-\delta R})$.

Theorem 3.5. Suppose that (3.4) holds. Let E_∞ be a "nondegenerate" eigenvalue of $H_\infty^{(W)}$ for some W, and let $E(R)$ be the eigenvalue $H^{(W_i)}(R)$ converging to E_∞. Then there exist $a_1, a_2,\ldots$, so that for any N, we have

$$E(R)-E_\infty-\sum_{n=1}^{N}a_nR^{-n}=O(R^{-N-1}) \tag{3.10}$$

as $R\to\infty$.

Proof. By (3.9), we can find $\gamma\in\mathscr{H}_a$, an eigenfunction of H_a, so that $E(R)$ can be written in terms of

$$(I_R\gamma,[H(R)-z]^{-1}I_R\gamma) \tag{3.11}$$

so it suffices to obtain an asymptotic series for (3.11).

On $\mathscr{H}_a$, define

$$\tilde{Y}(R) = -\sum_{i\in C_0(a)} Z_B|r_i - R\hat{e}|^{-1} - \sum_{i\in C_1(a)} Z_A|r_i + R\hat{e}|^{-1} + \sum_{i\in C_0(a), j\in C_1(a)} |r_i - r_j - R\hat{e}|^{-1}.$$

I_R is a unitary map of $\mathscr{H}_a$ onto $L^2(\mathbb{R}^{3N})$ and

$$H(R)I_R = I_R(H_a + \tilde{Y}(R)).$$

Thus,

$$(I_R\gamma, [H(R)-z]^{-1}I_R\gamma) = (\gamma, [H_a + \tilde{Y}(R) - z]^{-1}\gamma) \equiv f(R).$$

Using the exponential falloff of γ, one sees easily that

$$\|[\tilde{Y}(R)(H_a - z)^{-1}]^M\gamma\| \le C_M R^{-M}.$$

Thus, we get

$$f(R) = \sum_{n=0}^{N} (\gamma, (H_a - z)^{-1}[-\tilde{Y}(R)(H_a - z)^{-1}]^n\gamma) + O(R^{-N-1}).$$

Now expand $Y(R)$ in a multipole expansion. Explicitly, we get

$$\tilde{Y}(R) = \sum_{j=1}^{K} R^{-j}A_j + B_K(R),$$

where

$$\|(-\Delta+1)^{-1/2}B_K(R)(-\Delta+1)^{-1/2}e^{-a|x|}\| = O(R^{-K-1}).$$

Thus, $f(R)$ has an asymptotic expansion. ∎

Remark. The a_n's are thus given by perturbation theory in a multipole expansion. The usual arguments then lead to a calculation of the leading behavior, e.g., if both clusters are neutral and have no dipole moments or quadrupole moment then the leading behavior is a second-order dipole, i.e., $O(R^{-6})$ [20, pp. 319–322].

We close this section with an indication of what to do when (3.4) fails. It pays to bear an explicit example in mind, say a case with $N=3$. Let a be the decomposition with $C_0(a)=\{1,2\}$, and let W be the totally antisymmetric space. If the continuum for H_∞ is determined by an eigenvalue of $H_{12}^{(A)}$ which is symmetric under interchange and for $H_\infty^{(W)}$ by an eigenvalue of $H_{12}^{(A)}$ which is antisymmetric, then there can be an eigenvalue E_∞ of $H_\infty^{(W)}$ with $\mu_\infty(H_\infty) < E_\infty < \mu_\infty(H_\infty^{(W)})$.

In the general situation, pick some a with $\eta_a \ne 0$. In the above case $C_0(a) = \{1, 2\}$. Let $W^{(a)}$ be the representation of the subgroup of the symmetric group which does not interchange any electrons between $C_0(a)$ and $C_1(a)$. $W^{(a)}$ is not in general irreducible, $W^{(a)} = W_1^{(a)} \oplus \cdots \oplus W_k^{(a)}$. In the above special case, $W^{(a)}$ involves antisymmetry between 1 and 2 only; it is irreducible. Let $H_a^{(W)}$ denote the restriction of H_a to all vectors transforming under some $W_i^{(a)}$. It is easy to see that

$$\sigma(H_a^{(W)}) \subset \sigma(H_\infty^{(W)}),$$

and, in particular,

$$E_\infty < \mu_\infty(H_\infty^{(W)}) \le \mu_\infty(H_a^{(W)}).$$

Now we proceed as follows: Let $\tilde{P}(R)$ be the projection onto the eigenspace of $H(R)$ restricted to the subspace of symmetry $W^{(a)}$. Then, we get

$$E(R) = (I_R\eta_a, H(R)\tilde{P}(R)I_R\eta)/(I_R\eta_a, \tilde{P}(R)I_R\eta).$$

By writing

$$(I_R\eta_a, \tilde{P}(R)I_R\eta) = (I_R\hat{P}(R)\eta_a, I_R\eta),$$

with $\hat{P}(R)$ the projection onto the eigenspace for $H_a + \tilde{Y}(R)$ restricted to the $\mathscr{H}_a^{(W_a)}$, we can replace η by η_a with only an error of $O(e^{-\delta R})$. Then the argument proceeds as in the case where (3.4) holds except we always deal with H_a restricted to $\mathscr{H}_a^{(W_a)}$ rather than the full H_a.

4. Coefficients of the $1/R$ Expansion

After one has proved that the $1/R$ series is asymptotic, it is natural to enquire whether the series approximates the function in a stronger sense. For simplicity, we will study the $1/R$ expansion for the ground state ($1\,^2\Sigma_g^+$) of H_2^+. We shall derive a rigorous upper bound to the $|a_n|$'s and shall present numerical evidence that the series is neither convergent for small $1/R$ nor even Borel summable. In fact, the nth coefficient a_n appears to grow like $-C_0(n+1)!/2^{n+1}$.

As we have mentioned in Sec. 1, there is a close analogy between these results and recent results [13, 14] on the double-welled anharmonic oscillator $p^2+x^2+2gx^3+g^2x^4$. In that case too the perturbation coefficients grow like $(n+\alpha)!\beta^n$ for suitable α, β (numerical, not rigorous). In the anharmonic oscillator, the β that arises is connected to the γ which occurs in the asymptotics of the gap $\Delta E(g)$ between the two lowest eigenvalues via $(\Delta E)(g) = Cg^\delta \exp(-\gamma/g^2)$ by $\gamma = 2\beta$. In our case, the $1/2^n$ is presumably related to the fact that the gap in H_2^+ behaves like $c\exp(-R)$ [16, 21].

If the degeneracy of the double well is removed by replacing $p^2+x^2+2gx^3+g^2x^4$ by $p^2+(1+\varepsilon)x^2+2gx^3+g^2x^4$, then the resulting perturbation series is Borel summable [22]. This might lead one to suspect that the series for the ground state of $-\Delta - r^{-1} - \zeta|r-R|^{-1}$ is Borel summable for $\zeta<1$. However, the proof for the oscillator [22] does not extend to this case and numerical analysis of the coefficients using the methods of the Appendix suggest that for $0<\zeta<1$ there is still a singularity of the Borel transform on the positive real axis. There is some evidence for Borel summability if $\zeta<0$; indeed $a_n(\zeta=-1) = (-1)^n a_n(\zeta=1)$, so that numerically $a_n(\zeta=-1) \sim (-1)^n(n+1)!2^{n-1}$, which suggests Borel summability. We now turn to our detailed study of the coefficients of the $1/R$ expansion for the ground state in H_2^+.

Theorem 4.1. The coefficients a_n of the $1/R$ expansion of $E(R)$, the ground state of H_2^+, satisfy

$$|a_n| \le A^{n+1}n! \tag{4.1}$$

for a suitable constant A.

Proof. By Theorem 3.5 and its proof,

$$E(R)=[\phi, P(R)\phi]^{-1}(\phi, H(R)P(R)\phi)+\cdots,$$

where the dots denote exponential errors, $H(R)=H_0+V(R)$, $H_0=-\Delta^2-1/r$, $V(R)=-|R-r|^{-1}+R^{-1}$, where

$$P(R)=(2\pi i)^{-1}\oint_{|E-E_0|=\varepsilon}[E-H(R)]^{-1}\,dE$$

and ϕ is the ground state $(1s)$ of H_0. Moreover, as in that proof,

$$(H(R)\phi, P(R)\phi)=\sum_{n=0}^{N} b_nR^{-n}+O(R^{-N-1}),$$

$$(\phi, P(R)\phi)=\sum_{n=0}^{N} c_nR^{-n}+O(R^{-N-1}).$$

It is easy to see since $c_0\neq 0$ that it suffices to prove an estimate of the form (4.1) separately for the b_n and c_n. We consider the latter case; the situation for b_n is similar.

Expand $V(R)$ in a formal multipole expansion $V(R)\simeq\sum_{n=2}^{\infty}M_nR^{-n}$. M_n is an unbounded multiplication operator bounded by r^{n-1}, i.e., $|M_n\phi|\leq r^{n-1}|\phi|$ pointwise. By expanding $[E-H(R)]^{-1}=[E-H_0-V(R)]^{-1}$ in a geometric series as in Theorem 3.5, we see that c_n is a contour integral of a sum of terms of the form

$$(\phi, (E-H_0)^{-1}M_{k_1}(E-H_0)^{-1}\cdots M_{k_l}(E-H_0)^{-1}\phi), \tag{4.2}$$

with $k_1+\cdots+k_l=n$. The number of such terms is dominated by the number of distinct ways of decomposing n as a sum $j_1+\cdots+j_n$ with $j_i\geq 0$, i.e., $\binom{2n-1}{n-1}$. Thus, the number of terms is certainly dominated by 4^n and thus we need only prove a bound of form (4.1) for each term of the form (4.2).

We now borrow an argument of Avron et al. [23] used to obtain a similar bound for the Zeeman coefficients. As explained in Sec. 3, we can find some numbers, $C, D>0$ so that

$$\|e^{-\delta r}(H_0-E)^{-1}e^{+\delta r}\|\leq C \tag{4.3}$$

for all $|\delta|\leq D$ and E with $|E-E_0|=\varepsilon$ and so that

$$\|e^{Dr}\phi\|\leq C. \tag{4.4}$$

Now write

$$(E-H_0)^{-1}M_{k_1}\cdots M_{k_l}(E-H_0)^{-1}\phi=T_0S_1T_1\cdots T_l e^{Dr}\phi, \tag{4.5}$$

with

$$S_i=M_{k_i}\exp(-k_iDr/n)\quad\text{and}\quad T_i=e^{j_iDr/n}(H_0-E)^{-1}e^{-j_iDr/n},$$

with

$$j_i=\sum_{s=1}^{i}k_s.$$

Note that $\|T_i\|\leq C$ and since M_kr^{-k+1} is bounded, we get

$$\|S_i\|\leq n^{k_i-1}C_0^{k_i}$$

for some constant C_0, since

$$\sup_{r>0}\|r^{k-1}e^{-kDr/n}\|=\sup_{y>0}n^{k-1}\|y^{k-1}e^{-Dy}\|\leq n^{k-1}\left(\sup_{y>0}\|(1+y)e^{-Dy}\|\right)^k.$$

TABLE I. $1/R$ coefficients for H_2^+.

i	$-a_i$	a_i/a_{i-1}	$-a_i\cdot 2^{i+1}/(i+1)!$
0	0.5	-	1.0
1	0.0	0.0	0.0
2	0.0	-	0.0
3	0.0	-	0.0
4	2.25	-	0.6
5	0.0	0.0	0.0
6	7.5	-	0.190476
7	5.325 x10	7.1	0.338095
8	1.21172 x10^{2}	2.27553	0.170966
9	8.865 x10^{2}	7.31605	0.250159
10	5.29744 x10^{3}	5.97568	0.271794
11	2.90547 x10^{4}	5.48467	0.248450
12	2.04640 x10^{5}	7.04327	0.269215
13	1.44383 x10^{6}	7.05544	0.271348
14	1.08898 x10^{7}	7.54321	0.272878
15	8.83673 x10^{7}	8.11470	0.276791
16	7.55200 x10^{8}	8.54615	0.278294
17	6.83126 x10^{9}	9.04563	0.279705
18	6.51458 x10^{10}	9.53644	0.280778
19	6.53080 x10^{11}	10.02489	0.281476
20	6.86982 x10^{12}	10.51911	0.281988
21	7.56566 x10^{13}	11.01289	0.282319
22	8.70701 x10^{14}	11.50859	0.282530
23	1.04525 x10^{16}	12.00468	0.282640
24	1.30676 x10^{17}	12.50190	0.282683
25	1.69870 x10^{18}	12.99932	0.282668
26	2.29282 x10^{19}	13.49750	0.282616
27	3.20898 x10^{20}	13.99577	0.282531
28	4.65127 x10^{21}	14.49454	0.282424
29	6.97382 x10^{22}	14.99337	0.282300
30	1.08042 x10^{24}	15.49253	0.282164
31	1.72778 x10^{25}	15.99172	0.282018
32	2.84931 x10^{26}	16.49115	0.281866
33	4.84114 x10^{27}	16.99058	0.281710
34	8.46724 x10^{28}	17.49019	0.281552
35	1.52324 x10^{30}	17.98980	0.281393
36	2.8164 x10^{31}	18.48953	0.281233
37	5.34813 x10^{32}	18.98926	0.281074
38	1.04230 x10^{34}	19.48906	0.280917

Thus, each term of the form (4.2) is dominated by

$$(C+L)^{n+2}C_0^n n^n \leq A^{n+1} n!$$

for suitable A. ∎

We have calculated the first 39 a_n's of the $1/R$ expansion for the ground state of H_2^+. Our results appear in column 1 of Table I. Our computational methods are described in the Appendix. Our results agree with the previous work of Dalgarno and Stewart [24], who carried out the computation as far as a_{11}. [Coulson [25] reported an incorrect value for a_{10}, which was repeated in Ref. 26 (corrected in Ref. 24) and quite recently in Ref. 28.]

For $i \leq 11$, the ratio a_i/a_{i-1} (given in column 2 of Table I) is not steadily increasing, so it would have been premature on the basis of such a low order calculation to conclude that the series $\sum_{i=0}^{\infty} a_i R^{-i}$ diverges for all $R^{-1}>0$. If anything, the decrease of the ratio for $i=9$, 10, 11 suggests that the series might actually converge for sufficiently small R^{-1}. It is only for $i \geq 13$ that one sees the linear growth in the ratio which implies divergence for all $R^{-1}>0$. Indeed, one sees fairly strong evidence for convergence of the ratio to $\frac{1}{2}(i+1)$ which suggests the *Ansatz* $a_i \sim (i+1)!2^{i+1}$. The normalized quantities

$$N_i = -a_i 2^{i+1}/(i+1)!$$

are listed in column 3 of Table I. These quantities steadily increase for $11 \leq i \leq 24$ and then decrease at an accelerating rate for $24 \leq i \leq 39$, the limit of our calculation. We thus appear to still be sufficiently far from "asymptopia" to find reliable values for numbers c_i in the natural *Ansatz*

$$N_n \sim c_0 + c_1/n + c_2/n^2 + \cdots,$$

although one would expect that c_0 lies somewhere between 0.24 and 0.30.

Appendix: Recursive Calculation of the Coefficients of the $1/R$ Expansion for H_2^+

Here we outline the recursive procedure used to generate the results of Table I. Our analysis takes off from the idea of Coulson [25] to expand the perturbed wave functions in terms of generalized Laguerre functions and Legendre polynomials.

With

$$H_0 = -\tfrac{1}{2}\nabla^2 - 1/r, \quad E_0 = -\tfrac{1}{2},$$
$$\psi_0 = c_{00}^0 e^{-r} (c_{00}^0 = 1), \tag{A.1}$$

and

$$H = H_0 - \sum_{i=1}^{\infty} \frac{r^i}{R^{i+1}} P_i(\cos\theta),$$

$$\psi = \psi_0 + \sum_{j=1}^{\infty} \frac{1}{R^j} \psi_j, \tag{A.2}$$

the perturbative equations for $i \geq 2$ are

$$(H-E_0)\psi_i = \sum_{j=0}^{i-1} E_{i-j}\psi_j + \sum_{j=0}^{i-2} r^{i-j-1} P_{i-j-1}(\cos\theta)\psi_j. \tag{A.3}$$

For $j \geq 1$, write ψ_j as

$$\psi_j = \sum_{l=0}^{j-1} \sum_{k=0}^{j-l} \frac{(j-l)!}{2^{j-l}} c_{lk}^j z^l L_k^{2l+1}(z) P_l(\cos\theta)\, e^{-z/2}, \tag{A.4}$$

where $z=2r$. The factor of $(j-l)!/2^{j-l}$ is useful computationally for preventing the c_{lk}^j's from increasing too rapidly. Following Coulson, $E_1=0$, $E_2=0$, and we may take $\psi_1 \equiv 0$.

In order for (A.3) to have a solution, it is necessary that the right-hand side of (A.3) be orthogonal to ψ_0. Thus

$$E_i = -\left(\int \psi_0^2\right)^{-1} \left(\sum_{j=1}^{i-2} E_{i-j} \int \psi_j\psi_0 + \sum_{j=1}^{i-2} \int r^{i-j-1} P_{i-j-1}\psi_j\psi_0\right). \tag{A.5}$$

Using (A.4) to expand the ψ_j's, it follows that

$$\begin{aligned} E_i = -\frac{1}{2}\Bigg(&\sum_{j=1}^{i-2} \frac{j!}{2^j} E_{i-j} \sum_{k=0}^{j} c_{0k}^j \int_0^\infty dz\, z^2 L_k^1(z) L_0^1(z)\, e^{-z} \\ &+ \sum_{j=1}^{i-2} \sum_{l=0}^{j-1} \sum_{k=0}^{j-l} \frac{(j-l)!}{2^{j-l}} \frac{1}{2} \int_{-1}^{1} d(\cos\theta) P_{i-j-1}(\cos\theta) P_l(\cos\theta) c_{lk}^j \\ &\times \int_0^\infty dz\, z^2 z^l \frac{z^{i-j-1}}{2^{i-j-l}} L_k^{2l+1}(z)\, e^{-z}\Bigg). \end{aligned} \tag{A.6}$$

The integral of Legendre polynomials is $\delta_{l,i-j-1}[2/(2i-2j-1)]$. Thus

$$\begin{aligned} E_i = -\frac{1}{2}\Bigg(&\sum_{j=1}^{i-2} \frac{j!}{2^j} E_{i-j} \sum_{k=0}^{j} c_{0k}^j \int_0^\infty dz\, z^2 L_k^1(z) L_0^1(z)\, e^{-z} \\ &+ \sum_{j=i/2}^{i-2} \frac{1}{2i-2j-1} \frac{(2j-i+1)!}{2^{2j-i+1}} \sum_{k=0}^{2j-i+1} c_{i-j-1,k}^j \\ &\times \int_0^\infty dz\, z^2 \frac{z^{2i-2j-2}}{2^{i-j-1}} L_k^{2i-2j-1}(z) L_0^{2i-2j-1}(z)\, e^{-z}\Bigg). \end{aligned} \tag{A.7}$$

Since [27, Eq. 8.971.6]

$$z L_0^\alpha(z) = -L_1^\alpha(z) + (\alpha+1) L_0^\alpha(z), \tag{A.8}$$

$$\begin{aligned} E_i = -\frac{1}{2}\Bigg(&\sum_{j=1}^{i-2} \frac{j!}{2^j} E_{i-j} \sum_{k=0}^{j} c_{0k}^j \int_0^\infty dz\, z L_k^1(z)[2L_0^1(z) - L_1^1(z)]\, e^{-z} \\ &+ \sum_{j=i/2}^{i-2} \frac{1}{2i-2j-1} \frac{(2j-i+1)!}{2^i} \sum_{k=0}^{2j-i+1} c_{i-j-1,k}^j \\ &\times \int_0^\infty dz\, z^{2i-2j-1} L_k^{2i-2j-1}(z)[(2i-2j) L_0^{2i-2j-1}(z) - L_1^{2i-2j-1}(z)]\, e^{-z}\Bigg) \end{aligned}$$

$$= -\frac{1}{2}\Bigg(\sum_{j=1}^{i-2} \frac{j!}{2^j} E_{i-j}(2c_{00}^i - 2c_{01}^i) + \sum_{j=i/2}^{i-2} \frac{1}{2i-2j-1} \frac{(2j-i+1)!}{2^i}$$

$$\times [(2i-2j)(2i-2j-1)! c_{i-j-1,0}^i - (2i-2j)! c_{i-j-1,1}^i]\Bigg)$$

$$= -\Bigg(\sum_{j=1}^{i-2} \frac{j!}{2^j} E_{i-j}(c_{00}^i - c_{01}^i) + \sum_{j=i/2}^{i-2} \frac{(2j-i+1)!(i-j)!(2i-2j-3)!!}{2^{2j-i}}$$

$$\times (c_{i-j-1,0}^i - c_{i-j-1,1}^i)\Bigg), \qquad \text{(A.9)}$$

where we have used [27, Eq. 7.414.3] to evaluate the integrals. It is straightforward to see that

$$\frac{z}{2}(H - E_0)\psi_i = \sum_{l=0}^{i-1} \sum_{k=0}^{i-l} c_{lk}^i \frac{(i-l)!}{2^{i-l}} (k+l) P_l(\cos\theta) z^l L_k^{2l+1}(z)\, e^{-z/2}, \qquad \text{(A.10)}$$

and that

$$\sum_{j=0}^{i-1} E_{i-j}\psi_j = E_i c_{00}^0 P_0(\cos\theta) L_0^1(z)\, e^{-z/2}$$

$$+ \sum_{l=0}^{i-2} \sum_{k=0}^{i-l-1} \sum_{j=l+\max(1,k)}^{i-1} E_{i-j} \frac{(j-l)!}{2^{j-l}} c_{lk}^j P_l(\cos\theta) z^l L_k^{2l+1}(z)\, e^{-z/2}, \qquad \text{(A.11)}$$

so by [27, Eq. 8.971.6]

$$\frac{z}{2}\sum_{j=0}^{i-1} E_{i-j}\psi_j = E_i c_{00}^0 P_0(\cos\theta)[L_0^1(z) - \tfrac{1}{2}L_1^1(z)]\, e^{-z/2}$$

$$- \sum_{l=0}^{i-2} \sum_{k=1}^{i-l} \frac{k}{2} \sum_{j=l+\max(1,k-1)}^{i-1} \frac{(j-l)!}{2^{j-l}} c_{l,k-1}^j$$

$$\times P_l(\cos\theta) z^l L_k^{2l+1}(z)\, e^{z/2}$$

$$+ \sum_{l=0}^{i-2} \sum_{k=0}^{i-l-1} (k+l+1) \sum_{j=l+\max(1,k)}^{i-1} E_{ij} \frac{(j-l)!}{2^{j-l}} c_{l,k}^j$$

$$\times P_l(\cos\theta) z^l L_k^{2l+1}(z)\, e^{-z/2}$$

$$- \sum_{l=0}^{i-2} \sum_{k=0}^{i-l-2} \left(\frac{k}{2} + l + 1\right) \sum_{j=l+k+1}^{i-1} E_{i-j} \frac{(j-l)!}{2^{j-l}} c_{l,k+1}^j$$

$$\times P_l(\cos\theta) z^l L_k^{2l+1}(z)\, e^{-z/2}. \qquad \text{(A.12)}$$

Similarly,

$$\frac{z}{2}\sum_{j=0}^{i-2} r^{i-j-1} P_{i-j-1}(\cos\theta)\psi_j$$

$$= c_{00}^0 \frac{z^i}{2^i} P_{i-1}(\cos\theta) L_0^1(z)\, e^{-z/2}$$

$$+ \sum_{l=0}^{i-2} \sum_{j=1}^{i-2} \sum_{m=0}^{j-1} \sum_{n=0}^{j-m} (2l+1) c_{mn}^j \frac{(j-m)!}{2^{j-m}} \begin{pmatrix} l & i-j-1 & m \\ 0 & 0 & 0 \end{pmatrix}^2$$

$$\times P_l(\cos\theta) \frac{z^{i-j}}{z^{i-j}} z^m L_n^{2m+1}(z)\, e^{-z/2}, \qquad \text{(A.13)}$$

where we have used [20, Eq. (107.15)].

We need to express $z^{i-j+m} L_n^{2m+1}(z)\, e^{-z/2}$ as a linear combination of $z^l L_k^{2l+1}(z)\, e^{-z/2}$. We work in the space $L^2([0,\infty), z\,dz)$, in which these latter functions are orthogonal, and the square of their norms is $(2l+k+1)!/k!$. Expand (27, Eq. 8.970.2]

$$z^{i-j+m} L_n^{2m+1}(z)\, e^{-z/2} = z^{m+i-j} \sum_{p=0}^{n} (-1)^p \binom{n+2m+1}{n-p} \frac{z^p}{p!} e^{-z/2}, \qquad \text{(A.14)}$$

so by [27, Table Eq. 11]

$$\int_0^\infty dz\, z z^l L_k^{2l+1}(z)\, e^{-z/2} z^{m+i-j} L_n^{2m+1}(z)\, e^{-z/2}$$

$$= \sum_{p=0}^{n} (-1)^p \binom{n+2m+1}{n-p} \frac{1}{p!} \int_0^\infty dz\, e^{-z} z^{l+m+i-j+p+1} L_k^{2l+1}(z)$$

$$= \sum_{p=0}^{n} (-1)^p \binom{n+2m+1}{n-p} \frac{1}{p!} \frac{\Gamma(l+m+i-j+p+2)}{k!} \frac{\Gamma(l+k+j-m-p-i)}{\Gamma(l+j-m-p-i)}. \qquad \text{(A.15)}$$

The last ratio of Γ's is

$$(-1)^k[\Gamma(i-j+m-l+p+1)/\Gamma(i-j+m-l+p-k+1)], \qquad \text{(A.16)}$$

so

$$z^{i-j+m} L_n^{2m+1}(z)\, e^{-z/2} = \sum_{k=0}^{i-l} \sum_{p=0}^{n} (-1)^{p+k}$$

$$\times \binom{n+2m+1}{n-p} \frac{1}{p!} \frac{(l+m+i-j+p+1)!}{(2l+k+1)!}$$

$$\times \frac{\Gamma(i-j+m-l+p+1)}{\Gamma(i-j+m-l+p-k+1)} z^l L_k^{2l+1}(z)\, e^{-z/2}. \qquad \text{(A.17)}$$

Inserting this expression in (A.13) and using the fact that $L_0^{\alpha}(z)=L_0^1(z)$, we obtain

$$\frac{z}{2}\sum_{j=0}^{i-2} r^{i-j-1}P_{i-j-1}(\cos\theta)\psi_j = c_{00}^0\frac{z^i}{2^i}P_{i-1}(\cos\theta)L_0^{2i-1}(z)\,e^{-z/2}$$

$$+\sum_{l=0}^{i-2}\sum_{k=0}^{i-l}\sum_{j=1}^{i-2}\sum_{m=0}^{j-1}\sum_{n=0}^{j-m}\sum_{p=0}^{n}(-1)^{p+k}(2l+1)$$

$$\times c_{mn}^j\frac{(j-m)!}{2^{j-m}}\begin{pmatrix} l & i-j-1 & m\\ 0 & 0 & 0\end{pmatrix}^2$$

$$\times 2^{-i+j}\binom{n+2m+1}{n-p}\frac{1}{p!}\frac{(l+m+i-j+p+1)!}{(2l+k+1)!}$$

$$\times\frac{\Gamma(i-j+m-l+p+1)}{\Gamma(i-j+m-l+p-k+1)}z^lL_k^{2l+1}(z)\,e^{-z/2}. \tag{A.18}$$

The ranges of the summations can be reduced. For example, $\Gamma^{-1}(i-j+m-l+p+k+1)=0$ unless $k-i+j-m+l\le p\le n$. Also, the $3-j$ symbol vanishes unless $i-j-1\le l+m\le l+j-1$, i.e., $j\ge\frac{1}{2}(i-l)$.

We can now write down the recursive equations for the c_{lk}^i's by matching coefficients of the basis functions.

If $k=0$, $l=0$, we can set

$$c_{00}^i=0. \tag{A.19}$$

If $k=0$, $1\le l\le i-2$,

$$c_{l,0}^i=\frac{1}{l}\Bigg((l+1)\sum_{j=l+1}^{i-1}E_{i-j}\frac{(j-l)!}{(i-l)!}2^{i-j}(c_{l0}^j-c_{l1}^j)$$

$$+(2l+1)\sum_{j=(i-l)/2}^{i-2}\sum_{m=0}^{j-1}\sum_{n=0}^{j-m}\sum_{p=0}^{n}(-1)^pc_{mn}^j\frac{(j-m)!}{(i-l)!}$$

$$\times 2^{m-l}\begin{pmatrix} l & i-j-1 & m\\ 0 & 0 & 0\end{pmatrix}^2\binom{n+2m+1}{n-p}\frac{1}{p!}\frac{(l+m+i-j+p+1)!}{(2l+1)!}\Bigg), \tag{A.20}$$

and if $k=0$, $l=i-1$,

$$c_{i-1,0}^i=\frac{i}{i-1}\frac{1}{2^{i-2}}c_{00}^0. \tag{A.21}$$

If $l\le i-3$ and $1\le k\le i-l-2$

$$c_{lk}^i=\frac{1}{k+l}\Bigg(-\frac{k}{2}\sum_{\substack{j=l+\max(1,k-1)\\-\delta_{l,0}\delta_{k,1}}}^{i-1}E_{i-j}\frac{(j-l)!}{(i-l)!}2^{i-j}c_{l,k-1}^j$$

$$+(k+l+1)\sum_{j=l+k}^{i-1}E_{i-j}\frac{(j-l)!}{(i-l)!}2^{i-j}c_{lk}^j$$

$$-\left(\frac{k}{2}+l+1\right)\sum_{j=l+k+1}^{i-1}E_{i-j}\frac{(j-l)!}{(i-l)!}2^{i-j}c_{l,k+1}^j$$

$$+(2l+1)(-1)^k\sum_{j=(i-l)/2}^{i-2}\sum_{m=0}^{j-1}\sum_{n=\max(0,k-i+j-m+l)}^{j-m}$$

$$\times\sum_{p=\max(0,k-i+j-m+l)}^{n}(-1)^pc_{mn}^j\frac{(j-m)!}{(i-l)!}2^{m-l}\begin{pmatrix} l & i-j-1 & m\\ 0 & 0 & 0\end{pmatrix}^2$$

$$\times\binom{n+2m+1}{n-p}\frac{1}{p!}\frac{(l+m+i-j+p+1)!}{(2l+k+1)!}\frac{\Gamma(i-j+m-l+p+1)}{\Gamma(i-j+m-l+p-k+1)}\Bigg). \tag{A.22}$$

If $l\le i-2$ and $k=i-l-1$,

$$c_{l,i-l-1}^i=\frac{2l+1}{i-1}(-1)^{i-l-1}\sum_{j=(i-l)/2}^{i-2}\sum_{m=0}^{j-1}\sum_{n=j-m-1}^{j-m}$$

$$\times\sum_{p=j-m-1}^{n}(-1)^pc_{mn}^j\frac{(j-m)!}{(i-l)!}2^{m-l}+\begin{pmatrix} l & i-j-1 & m\\ 0 & 0 & 0\end{pmatrix}^2\binom{n+2m+1}{n-p}\frac{1}{p!}$$

$$\times\frac{(l+m+i-j+p+1)!}{(i+l)!}\frac{\Gamma(i-j+m-l+p+1)}{\Gamma(m-j+p+2)}. \tag{A.23}$$

If $l\le i-2$ and $k=i-l$,

$$c_{l,i-l}^i=\frac{(-1)^{i-l}}{i}\sum_{j=(i-l)/2}^{i-2}\sum_{m=0}^{j-1}(-1)^{j-m}c_{m,j-m}^j2^{m-l}\begin{pmatrix} l & i-j-1 & m\\ 0 & 0 & 0\end{pmatrix}^2. \tag{A.24}$$

If $l=i-1$,

$$c_{i-1,1}^i=-(1/i)(1/2^{i-1})c_{00}^0. \tag{A.25}$$

Notes added after refereeing. (i) The idea following Theorem 2.2 of using special J's so that (2.6) holds, an idea we attribute to Ref. 17, appears earlier in Ref. 30. (ii) We are grateful to the referee for emphasizing to us the beautiful differential equation methods in Ref. 28. (iii) Motivated by our preprint, Brezin and Zinn-Justin [31] have carried the analogy to the double well further. In a nonrigorous way, they derive an asymptotic formula $-C_0(n+1)!/2^{n+1}$ with $C_0=2/e^2=0.2706705665$ consistent with Table I, column 3.

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Bibliography

[1] R. Ahlrichs, Theor. Chim. Acta. **41**, 7 (1976).
[2] J. M. Combes and R. Seiler, Int. J. Quantum Chem. **14**, 213 (1978).

[3] P. Aventini and R. Seiler, Commun. Math. Phys. **41**, 119 (1975).
[4] V. Enss, Commun. Math. Phys. **52**, 233 (1977).
[5] B. Simon, Commun. Math. Phys. **55**, 259 (1977).
[6] B. Simon, Commun. Math. Phys. **58**, 205 (1978).
[7] V. Enss, Commun. Math. Phys. **61**, 285 (1978).
[8] M. Reed and B. Simon, *Methods of Modern Mathematical Physics, IV: Analysis of Operators* (Academic, New York, 1978).
[9] B. Simon, Helv. Phys. Acta **43**, 607 (1970).
[10] E. Balslev, Ann. Phys. New York. **73**, 49 (1972).
[11] B. Simon, Phys. Lett. A **71**, 211 (1979).
[12] B. Simon, Ann. Phys. New York. (to be published).
[13] E. Brézin, G. Parisi, and J. Zinn-Justin, Phys. Rev. D **16**, 408 (1977).
[14] E. Harrell, Commun. Math. Phys. **60**, 73 (1978).
[15] E. Harrell, Ann. Phys. (New York) **119**, 351 (1979).
[16] R. Damburg and R. Propin, J. Phys. B **1**, 681 (1968).
[17] J. Morgan, J. Operator Theory **1**, 109 (1979).
[18] F. Rellich, Math. Ann. **113**, 606 (1937).
[19] J. Combes and L. Thomas, Commun. Math. Phys. **34**, 251 (1973).
[20] L. Landau and E. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory* (Pergamon, New York, 1965).
[21] E. Harrell, Commun. Math. Phys. (to be published).
[22] B. Simon (unpublished).
[23] J. Avron, I. Herbst, and B. Simon, Comm. Math. Phys. (to be published).
[24] A. Dalgarno and A. Stewart, Proc. R. Soc. Lond. Ser. A **238**, 276 (1956).
[25] C. A. Coulson, Proc. R. Soc. Edinburgh, Sec. A **61**, 20 (1941).
[26] A. Dalgarno and J. Lewis, Proc. Phys. Soc. Lond. Ser. A **69**, 57 (1956).
[27] I. Gradshteyn and I. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1965).
[28] I. Komarov, L. Ponomarev, S. Slavyanov, *Spheroidalniye i Kulonovskie Spheroidalniye Funktsii* (Nauka, Moscow, 1976), p. 220.
[29] T. Kato, *Perturbation Theory for Linear Operators* (Springer, Berlin, 1966).
[30] R. Ismagilov, Sov. Math. Dokl. **2**, 1137 (1961).
[31] E. Brezin and J. Zinn-Justin, J. Phys. (Paris) **40**, L-511 (1979).

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Note added in proof: The figures presented in Table I supersede those in a preprint of this article, the last few of which apparently suffered from accumulating roundoff errors in the last few digits. The numbers in Table I agree with those obtained by J. Cizek, M. Clay, and J. Paldus in an independent calculation. We thank J. Cizek for telling us about their work.