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LETTER TO THE EDITOR

Rigorous bounds on eigenvalues of two-electron atomic Hamiltonians

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Abstract. Upper and lower bounds on the first two energy levels of atomic two-electron systems within various symmetry sectors are calculated. These bounds are mathematically completely rigorous because no uncontrolled numerical approximations are involved. The explicit and simple form of these bounds allows their application as input for further analytical manipulations. Examples of such applications are given for the problem of level ordering and the absorption of bound states into the continuum.

In the non-relativistic Schrödinger theory helium-like two-electron systems are described (in the infinite nuclear mass limit) by the Hamilton operator

$$H(Z)=\sum_{i=1}^{2}\left(-\frac{\Delta_i}{2}-\frac{Z}{r_i}\right)+\frac{1}{r_{12}} \tag{1}$$

(atomic units, $r_{12}:=|\boldsymbol{r}_1-\boldsymbol{r}_2|$) acting in the Hilbert space given by the antisymmetric tensor product $(L^2(\mathcal{R}^3)\otimes\mathcal{C}^2)\bigotimes_{\mathrm{A}}(L^2(\mathcal{R}^3)\otimes\mathcal{C}^2)$. The Hamiltonian H commutes with the total orbital angular momentum $\boldsymbol{L}=\boldsymbol{L}_1+\boldsymbol{L}_2$, the total partity $P=P_1P_2$ and each of the two spin operators $\boldsymbol{S}_1, \boldsymbol{S}_2$. Therefore, the bound states of H are usually classified into the different symmetry sectors ${}^{2S+1}L$ in which each state is characterised by its quantum numbers L and S.

The Schrödinger equation for (1) constitutes certainly one of the most intensely studied problems in the theory of atoms; consequently, for (1) also the most accurate approximations are available. In case of the helium atom approximate energies of its lowest states have been computed (Frankowski and Pekeris 1966, Kono and Hattori 1984, Freund *et al* 1984, Baker *et al* 1987) up to a precision including 14 or 15 significant digits and which are believed to be of some orders of magnitude more 'accurate' than the experimental data. But at this point the question of the meaning of 'accuracy' arises. Approximate values for which no strict error bounds are available may be useful for heuristical considerations; however, to employ them for establishing general theoretical statements would of course be a rather doubtful procedure.

The problem of bounding the eigenvalues of H includes two aspects. The first one is the theoretical derivation of the bounds, and the second involves their appropriate numerical realisation. For instance, variational computations of atomic energy levels should provide upper bounds to the exact values. But, on the other hand, the numerical procedure employed may be so complex that during the evaluation process round-off and other numerical errors add up in such a way that the final result actually lies below the true value. Although one could argue that on the average numerical errors

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tend to cancel each other, from a rigorous point of view such a situation is rather unsatisfactory. In particular, this type of result cannot be used for the derivation of mathematically rigorous statements.

This letter is intended as a first step to overcome the unsatisfactory situation described above. Our aim is to provide bounds on various energy levels of (1) which are not only mathematically rigorous and simple enough to be applicable for further analytical calculations, but also sufficiently sharp to be useful for deriving non-trivial qualitative results.

In fact, our bounds are mathematically rigorous because they are derived without any uncontrolled approximation. Although done on a computer, all calculations have been performed with the help of the symbolic calculus REDUCE. Due to the capability of REDUCE to handle integer arithmetic with arbitrary precision (Hearn 1985), and because all steps and estimates contain only rational manipulations, the final results are either exact or based on completely rigorous estimates.

Such estimates are in general necessary to achieve our second goal, namely simplicity. As it turns out, the exact values are fractions with numerators and denominators containing up to 90-digit integers. Since such quantities are of course not very practicable for further calculations, and since they themselves are already bounds, we have estimated them further by rational expressions which are subject to the condition that the denominator contains at most three digits. Compared with the sharpness of the exact bounds, these additional estimates do not induce any significant loss of accuracy. For the helium atom our bounds differ by less than a few per cent from those approximate values mentioned before and obtained via extensive numerical computations.

In the following we shall derive bounds on the two lowest energy levels E_1, E_2 within fixed symmetry sectors, $E_1 \leqslant E_2 \leqslant \ldots$ denoting the ordered sequence of elements of the discrete spectrum of H restricted to the respective symmetry subspace. Some of these bounds have been computed numerically before (Grosse *et al* 1978, Thirring 1981). If we convert our rational expressions into floating point numbers, they agree with those already existing bounds and thus provide a sound justification of them which should also satisfy a mathematical purist.

To derive lower bounds on the E_i we employ the well known method of intermediate operators (Weinstein and Stenger 1972). It rests on the fact that if P is any projector in the considered (sub-)space, then as operators $r_{12}^{-1} \geqslant r_{12}^{-1/2} P r_{12}^{-1/2}$ and consequently $H^{\mathrm{LB}} := H^{\mathrm{B}} + r_{12}^{-1/2} P r_{12}^{-1/2}$ is a lower bound operator on H, i.e. $H^{\mathrm{LB}} \leqslant H$. The ordering theorem then implies that the ordered sequence of points of the spectrum of H^{LB} provides lower bounds for the spectrum of H, that is $E_i^{\mathrm{LB}} \leqslant E_i$ for $i = 1, 2, \ldots$. Here H^{B} is the operator of the associated 'base problem'

$$H^{\mathrm{B}}(Z) = \sum_{i=1}^{2} \left(-\frac{\Delta_i}{2} - \frac{Z}{r_i} \right) \tag{2}$$

which is of hydrogenic type. Its eigenfunctions ψ_i^{B} and eigenvalues E_i^{B} can be expressed in terms of the usual hydrogenic functions ϕ_{nlm} (associated with the quantum numbers n, l, m) and hydrogenic energies (Balmer formula).

For the projector P we will adopt the choice introduced by Basley and Fox (1961, 1962), i.e. we take

$$P_N := \sum_{i,j=1}^{N} r_{12}^{1/2} |\psi_i^{\mathrm{B}}\rangle M_{ij}^{\mathrm{L}} \langle \psi_j^{B}| r_{12}^{1/2}$$

where the matrix elements M^{L}_{ij} of the matrix M^{L} serve as the normalisation coefficients. M^{L} is the inverse $M^{\mathrm{L}} = W^{-1}$ of the matrix W whose elements are given by $W_{ij} = \langle \psi^{\mathrm{B}}_i, r_{12}\psi^{\mathrm{B}}_j \rangle$. With this choice of P, for a given $N < \infty$, the resulting H^{LB}_N acts non-trivially only in an N-dimensional subspace. Therefore, for $N \leqslant 4$, in principle it is possible to obtain explicit expressions for its eigenvalues. For $N = 3$ or $N = 4$ this requires the computation of the roots of a polynomial of third or fourth degree and leads to unnecessary complex expressions without increasing the quality of the bounds significantly, and so we will use here only one- and two-dimensional projectors. Thus, lower bounds follow which in the one-dimensional case are of the form

$$E_1(Z) \geqslant \min\{E^{\mathrm{B}}_1(Z) + Z/M^{\mathrm{L}}_{11},\ E^{\mathrm{B}}_2(Z)\}. \tag{3}$$

A two-dimensional projector yields

$$\begin{aligned} E_1(Z) &\geqslant \min\{\varepsilon_-(Z),\ E^{\mathrm{B}}_3(Z)\} \\ E_2(Z) &\geqslant \min\{\varepsilon_+(Z),\ E^{\mathrm{B}}_3(Z)\} \end{aligned} \tag{4}$$

where

$$\varepsilon_\mp(Z) = A_1 Z^2 + B_1 Z \mp Z(A_2 Z^2 + B_2 Z + C)^{1/2} \tag{5a}$$

and

$$\begin{aligned} A_1 &= \tfrac{1}{2}(E^{\mathrm{B}}_1 + E^{\mathrm{B}}_2) & A_2 &= \tfrac{1}{4}(E^{\mathrm{B}}_1 - E^{\mathrm{B}}_2)^2 \\ B_1 &= \tfrac{1}{2}(M^{\mathrm{L}}_{11} + M^{\mathrm{L}}_{22}) & B_2 &= \tfrac{1}{2}(E^{\mathrm{B}}_1 - E^{\mathrm{B}}_2)(M^{\mathrm{L}}_{11} - M^{\mathrm{L}}_{22}) \\ C &= \tfrac{1}{4}(M^{\mathrm{L}}_{11} - M^{\mathrm{L}}_{22})^2 + (M^{\mathrm{L}}_{12})^2. \end{aligned} \tag{5b}$$

In the above formulae (3)-(5) we have extracted the Z dependence from the base energies E^{B}_i and matrix elements M^{L}_{ij} and have written the corresponding Z variables explicitly, i.e. the E^{B}_i and M^{L}_{ij} refer to a base problem (2) with $Z = 1$. The *minimum* in the lower bounds is a consequence of level crossing. As Z varies, there exist Z_{cross} such that for $Z \leqslant Z_{\mathrm{cross}}$ the lowest base level arising from the already diagonal part of H^{LB} is smaller than the level(s) from the non-trivial part.

Upper bounds on the E_i are obtained as a consequence of the 'minimax theorem' (Reed and Simon 1978) by diagonalising H within a subspace of sufficiently high dimensions. Here, in connection with the corresponding lower bound problem, we choose subspaces spanned by the symmetry adapted base functions ψ^{B}_i of (2) (cf table 1). Again, explicit expressions follow easily in the one-dimensional situation

$$E_1(Z) \leqslant E^{\mathrm{B}}_1 Z^2 + M^{\mathrm{U}}_{11} Z \tag{6}$$

and the two-dimensional situation

$$E_1(Z) \leqslant \varepsilon^{\mathrm{U}}_-(Z) \qquad E_2(Z) \leqslant \varepsilon^{\mathrm{U}}_+(Z) \tag{7}$$

Table 1. Base functions and eigenvalues for the various symmetry sectors.

	ψ^{B}_k	$E^{\mathrm{B}}_k(Z)$
^{1}S	$(\phi_{1,0,0} \otimes_{\mathrm{S}} \phi_{k,0,0}) \otimes$ {antisymmetric spin part}	$-\frac{1}{2}(1 + 1/k^2)Z^2$
^{3}S	$(\phi_{1,0,0} \otimes_{\mathrm{A}} \phi_{k+1,0,0}) \otimes$ {symmetric spin part}	$-\frac{1}{2}[1 + 1/(k+1)^2]Z^2$
^{1}P	$(\phi_{1,0,0} \otimes_{\mathrm{S}} \phi_{k+1,1,0}) \otimes$ {antisymmetric spin part}	
^{3}P	$(\phi_{1,0,0} \otimes_{\mathrm{A}} \phi_{k+1,1,0}) \otimes$ {symmetric spin part}	
$(^3\mathrm{P})_{\mathrm{unn}}$	$(\phi_{2,1,1} \otimes_{\mathrm{A}} \phi_{k+1,1,-1}) \otimes$ {symmetric spin part}	$-\frac{1}{2}[\frac{1}{4} + 1/(k+1)^2]Z^2$

where $\varepsilon_{\mp}^{U}$ are constructed analogously as $\varepsilon_{\mp}$ but contain the matrix elements $M_{ij}^{U} = \langle \psi_i^B, r_{12}^{-1} \psi_j^B \rangle$ instead of M_{ij}^{L}. Our results are summarised in the following theorem.

Theorem 1. For all positive Z the lowest energy levels of (1) restricted to the symmetry sectors ^1S, ^1P, ^3S, ^3P or $(^3P)_{unn}$, are bounded by (3)–(7) where the respective constants are given in table 2 (one-dimensional bounds) and table 3 (two-dimensional bounds). In particular, if $Z \geqslant Z_{cross}$, due to the concavity of $-(-E_1(Z))^{1/2}$ (Narnhofer and Thirring 1975) the linear one-dimensional bounds can be sharpened to parabolic ones

$$E_1^B(Z - Z_L)^2 \leqslant E_1(Z) \leqslant E_1^B(Z - Z_U)^2 \tag{8}$$

with the Z_L, Z_U of table 2.

Proof. We sketch the procedure for the ^1S symmetry, i.e. parahelium with vanishing angular momentum. First note that if $E_2(Z)$ or $E_1(Z)$ does not belong to the discrete

Table 2. Parameters of the linear and parabolic bounds for one-dimensional projections. Here $<$ or $>$ in front of an expression indicates that the exact quantity contains too many digits and has been estimated by the given bound according to the rules mentioned in the text. In the same way, if two numbers are given for Z_{cross}, they represent lower and upper bounds, respectively.

	^1S	^3S	^1P	^3P	$(^3P)_{unn}$
$1/M_{11}^{L}$	$\frac{16}{35}$	$>\frac{107}{670}$	$>\frac{120}{613}$	$>\frac{97}{522}$	$\frac{32}{231}$
M_{11}^{U}	$\frac{5}{8}$	$\frac{137}{729}$	$<\frac{204}{785}$	$<\frac{93}{412}$	$\frac{21}{128}$
Z_{cross}	$\frac{128}{105}$	$\frac{890}{387}, \frac{1803}{784}$	$\frac{2351}{834}, \frac{1339}{475}$	$\frac{1841}{688}, \frac{1453}{543}$	$\frac{768}{385}$
Z_L	$\frac{128}{105}(1-\sqrt{\frac{5}{8}})$	$\frac{58}{441}$	$\frac{133}{825}$	$\frac{101}{660}$	$\frac{768}{385}(1-\sqrt{\frac{13}{18}})$
Z_U	$\frac{5}{16}$	$<\frac{109}{725}$	$<\frac{179}{861}$	$<\frac{93}{515}$	$\frac{21}{64}$

Table 3. Parameters of the bounds for the two-dimensional projections. Except for the A_1 and A_2, which are exact, all other parameters are simplified bounds

	^1S	^3S	^1P	^3P	$(^3P)_{unn}$
A_1	$-\frac{13}{16}$	$-\frac{85}{144}$	$-\frac{85}{144}$	$-\frac{85}{144}$	$-\frac{31}{144}$
A_2	$(\frac{3}{16})^2$	$(\frac{5}{144})^2$	$(\frac{5}{144})^2$	$(\frac{5}{144})^2$	$(\frac{5}{144})^2$
B_1	$\frac{271}{849}$	$\frac{50}{413}$	$\frac{34}{235}$	$\frac{65}{471}$	$\frac{71}{655}$
Lower bound, ground state					
B_2	$-\frac{49}{859}$	$-\frac{3}{965}$	$-\frac{3}{707}$	$-\frac{3}{778}$	$-\frac{2}{877}$
C	$\frac{5}{196}$	$\frac{1}{404}$	$\frac{2}{437}$	$\frac{1}{268}$	$\frac{1}{777}$
Z_{cross}^{-}	$\frac{355}{353}, \frac{709}{705}$	$\frac{1133}{644}, \frac{431}{264}$	$\frac{1459}{749}, \frac{898}{461}$	$\frac{1293}{688}, \frac{1823}{970}$	$\frac{485}{334}, \frac{379}{261}$
Lower bound, first excited state					
B_2	$-\frac{17}{298}$	$-\frac{2}{643}$	$-\frac{2}{471}$	$-\frac{1}{259}$	$-\frac{1}{438}$
C	$\frac{24}{941}$	$\frac{2}{809}$	$\frac{3}{656}$	$\frac{3}{805}$	$\frac{1}{778}$
Z_{cross}^{+}	$\frac{1821}{740}, \frac{1319}{536}$	$\frac{3249}{992}, \frac{1559}{476}$	$\frac{1522}{413}, \frac{2447}{664}$	$\frac{1370}{383}, \frac{3459}{967}$	$\frac{253}{80}, \frac{2160}{683}$
Upper bound, ground state					
B_1	$\frac{386}{901}$	$\frac{99}{703}$	$\frac{145}{777}$	$\frac{133}{806}$	$\frac{81}{632}$
B_2	$-\frac{62}{841}$	$-\frac{3}{917}$	$-\frac{2}{393}$	$-\frac{1}{237}$	$-\frac{1}{401}$
C	$\frac{29}{531}$	$\frac{1}{266}$	$\frac{3}{308}$	$\frac{4}{661}$	$\frac{1}{522}$
Upper bound, first excited state					
B_2	$-\frac{23}{312}$	$-\frac{1}{306}$	$-\frac{5}{983}$	$-\frac{4}{949}$	$-\frac{2}{803}$
C	$\frac{42}{769}$	$\frac{3}{797}$	$\frac{8}{821}$	$\frac{5}{826}$	$\frac{1}{521}$

part $\sigma_{\text{dis}}(H(Z))$ of the spectrum $\sigma(H(Z))$, then we set $E_2(Z) := \inf\{\sigma(H(Z))\setminus\{E_1(Z)\}\}$ and $E_1(Z) := \inf\{\sigma(H(Z))\}$. In the ^{1}S subspace the base problem (2) has the solutions $\psi_i^{\text{B}} = (\phi_{1,0,0} \otimes_{\text{S}} \phi_{i,0,0}) \otimes$ (antisymmetric spin part) and the corresponding eigenvalues below the continuum $E_\infty^{\text{B}}(Z) = -Z^2/2$ are given by $E_n^{\text{B}}(Z) = -(1+1/n^2)Z^2/2$. The matrices W and M^{U} can be calculated with the help of our REDUCE procedures (Bogdanova and Hogreve 1987):

$$W = \begin{pmatrix} \frac{35}{16} & -\frac{123\,904}{194\,481} \\ -\frac{123\,904}{194\,481} & \frac{242\,909}{39\,366} \end{pmatrix} \qquad M^{\text{U}} = \begin{pmatrix} \frac{5}{8} & \frac{8192}{64\,827} \\ \frac{8192}{64\,827} & \frac{169}{729} \end{pmatrix}. \tag{9}$$

Inserting W_{11}^{-1} and M_{11}^{U}, the one-dimensional linear bounds follow immediately, and the parabolic ones from the general relation (Thirring 1981):

$$E_1^{\text{B}}\left(Z - \frac{1-(E_2^{\text{B}}/E_1^{\text{B}})^{1/2}}{(E_2^{\text{B}}-E_1^{\text{B}})\langle\psi_1^{\text{B}}, r_{12}\psi_1^{\text{B}}\rangle}\right)^2 \leqslant E_1(Z) \leqslant E_1^{\text{B}}\left(Z + \frac{\langle\psi_1^{\text{B}}, r_{12}\psi_1^{\text{B}}\rangle}{2E_1^{\text{B}}}\right)^2. \tag{10}$$

For the two-dimensional lower bounds we have to invert W. This can be done exactly, but already now the number of digits starts to proliferate:

$$M_{11}^{\text{L}} = \frac{22\,405\,152\,737\,744}{47\,537\,460\,297\,079} \qquad M_{22}^{\text{L}} = \frac{7942\,800\,465\,810}{47\,537\,460\,297\,079} \qquad M_{12}^{\text{L}} = M_{21}^{\text{L}} = \frac{2313\,309\,487\,104}{47\,537\,460\,297\,079}. \tag{11}$$

These M_{ij}^{L} have to be inserted into (5), but obviously the resulting lower bound expressions $\varepsilon_\mp$ will not be in a form inviting further applications. Hence we will refrain from displaying them here, but instead note that in (5*a*) the terms B_1, B_2 and C involving a large number of digits can be estimated by

$$\tfrac{271}{849} < B_1 < \tfrac{128}{401} \qquad -\tfrac{17}{298} < B_2 < -\tfrac{49}{859} \qquad \tfrac{24}{941} < C < \tfrac{5}{196}. \tag{12}$$

The estimates (12) can be verified by straightforward calculations; they are motivated by our desire to derive simpler but not much weaker bounds. The restriction to fractions whose denominators contain at most three digits allows an estimate of the actual values such that the difference does not exceed the order of 10^{-5} which is in fact some orders of magnitude better than the quality of the estimated bounds themselves. The analogous quantities for the upper bounds $\varepsilon_\mp^{\text{U}}$ are estimated in the same way.

The condition of level crossing is equivalent to a linear equation for Z_{cross} and to a quadratic equation for $Z_{\text{cross}}^\mp$. The roots of them can be determined exactly but eventually have to be estimated as above because they may contain too many digits to be of practical use.

In the same way the results for the other symmetry sectors are derived. Here, $(^3\text{P})_{\text{unn}}$ stands for the subspace of the ^{3}P sector with unnatural parity consisting of those states with $P = (-1)^{L+1}$. The lowest state with unnatural parity has $L = 1$ and antisymmetric spatial part, i.e. it belongs to the class of ortho systems, thus clarifying our choice of $(^3\text{P})_{unn}$.

As already emphasised, the bounds of theorem 1 are primarily intended to be employed in the derivation of certain qualitative properties of atomic systems (Briet *et al* 1987, Hogreve 1987). Here, as a further application of them, let us consider the problem of level ordering. The splitting of degenerate base levels under the influence of the electron–electron interaction is described by the well known rules of Hund (see Bethe and Jackiw 1980) which in our situation claim that

$$E_1(Z; {}^3\text{S}) \leqslant E_1(Z; {}^3\text{P}) \leqslant E_1(Z; {}^1\text{P}). \tag{13}$$

Although our bounds—neither in their simplified nor in their exact form—are sharp enough to prove the second inequality of (13), we can raise the first part of (13) to a theorem as follows.

Theorem 2. For all $Z \geqslant \frac{22}{13} \approx 1.6923$ we have

$$E_1^{\mathrm{UB}}(Z; {}^3\mathrm{S}) \leqslant E_1^{\mathrm{LB}}(Z; {}^3\mathrm{P}) \tag{14}$$

where the upper and lower bounds are those of theorem 1.

Proof. Inserting the respective values from table 3, the relation (14) becomes equivalent to $\sqrt{a+b} - \sqrt{a+c} \geqslant d$ where for $Z \geqslant Z_{\mathrm{cross}}^-$ we have $a = (\frac{5}{144}Z)^2$, $b = -\frac{3}{917}Z + \frac{3}{798}$, $c = -\frac{3}{778}Z + \frac{1}{268}$, $d = \frac{99}{703} - \frac{65}{471}$, and which in turn is equivalent to the non-negativity of a second-order polynomial:

$$p_2 Z^2 + p_1 Z + p_0 \geqslant 0. \tag{15}$$

Computing the p_i explicitly it is easy to see that (15) holds for all $Z \geqslant Z_{\mathrm{cross}}^-$, and, inserting the respective bounds for $Z \leqslant Z_{\mathrm{cross}}^-$, (15) is satisfied for all $Z \geqslant \frac{22}{13}$.

As a second example we want to apply our bounds to derive sufficient conditions on Z to guarantee the existence of bound states. A sufficient criterion for a wavefunction to represent a bound state of H, i.e. to be square integrable, is given if the corresponding energy does not belong to the essential spectrum of H. Here, we will deal with the threshold of the continuous part of $\sigma(H(Z))$ at $E_\infty(Z) = -\frac{1}{2}Z^2$ for the sector of natural parity, and $E_\infty^{\mathrm{unn}}(Z) = -\frac{1}{8}Z^2$ for the unnatural parity sector. The fact that the restriction of H to different symmetry subspaces gives rise to different 'ionisation energies' $E_\infty(Z)$ and $E_\infty^{\mathrm{unn}}(Z)$ implies the possible existence of (metastable) unnatural parity bound states with energies above $E_\infty(Z)$.

The absorption point Z_{abs} of the energy level $E(Z)$ into the continuum is defined by

$$E(Z_{\mathrm{abs}}) = E_\infty(Z_{\mathrm{abs}}) \tag{16}$$

and upper bounds on Z_{abs} guaranteeing bound states for $Z \geqslant Z_{\mathrm{abs}}^{\mathrm{UB}}$ are determined by

$$E^{\mathrm{UB}}(Z_{\mathrm{abs}}^{\mathrm{UB}}) = E_\infty(Z_{\mathrm{abs}}^{\mathrm{UB}}). \tag{17}$$

Theorem 3. (i) For all $Z \geqslant \frac{868}{901} \approx 0.9634$ the operator (1) has a discrete ground-state energy, and the associated ground state belongs to the ${}^1\mathrm{S}$ symmetry sector.

(ii) In the unnatural parity sector, H has a discrete ground-state energy (which is embedded in the continuum of the natural parity sector) for all $Z \geqslant \frac{1135}{996} \approx 1.1395$, and the associated ground state has ${}^3\mathrm{P}$ symmetry.

Proof. Employing the respective bounds E_1^{UB} from table 3, condition (17) becomes equivalent to a relation of the form (15). Calculating the p_i and estimating the lengthy expressions appropriately, the non-negativity of (15) holds for those Z given above.

With our bounds of theorem 1 and, more generally, with any lower bound functions derived from finite-dimensional Bazley–Fox projections, it is impossible to obtain necessary conditions for the existence of bound states, i.e. lower bounds $Z_{\mathrm{abs}}^{\mathrm{LB}}$ to Z_{abs}. This is due to the occurrence of crossings between the ε functions and the base levels. From the results of Lieb (1984) it is known that $H(Z)$ cannot have bound states for $Z \leqslant \frac{1}{2}$. Hence, in view of theorem 3(i), the Z range where the existence of a bound state is still not clear is given by the interval $(\frac{1}{2}, \frac{868}{901})$. From a non-linear variational treatment Stillinger and Stillinger (1974) have derived the upper bound $Z_{\mathrm{abs}}^{\mathrm{UB}} = 0.9538$,

and more recently, in the context of the $1/Z$ expansion, Baker *et al* (1987) have obtained $Z_{\text{abs}}^{\text{UB}} = 0.911\,03$ from a calculation based on 476 variational basic functions. Note that despite its simple form our rigorous bound is only about 5% higher. In particular our results are good enough to demonstrate rigorously the existence of H^-, at least in the sector of natural parity, whereas the standard variational upper bound $E_1^{\text{UB}} = -(Z - \frac{5}{16})^2$ would guarantee bound states only for $Z \geqslant \frac{5}{8}(1 + 1/\sqrt{2}) \approx 1.07$.

Since the work of Hill (1977) it is known that H^- has only one bound state in the natural parity subspace; a similar result holds in the unnatural parity sector (Grosse and Pittner 1983). Our bounds are not sharp enough to prove a discrete ground state with unnatural parity symmetry for H^-. Also the value $Z_{\text{abs}}^{\text{UB}} = 1.03$ from the non-linear variational calculus of Stillinger and Stillinger (1974) is not sufficient for this, whereas extrapolation of results from perturbation theory (Brändas and Goscinski 1972) gives evidence for the existence of an unnatural parity bound state until $Z = 0.9952$.

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