

# Binding limit in the Hartree approximation

Mary Beth Ruskai<sup>a)</sup> and Frank H. Stillinger  
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 8 November 1983; accepted for publication 23 December 1983)

We show that the Hartree approximation cannot predict that  $H^-$  has a bound state, i.e., the Hartree energy is greater than  $-0.5$ . We also show that the Hartree approximation cannot predict binding for the Coulomb model of a two-electron atom unless the nuclear charge  $Z$  is greater than 1.03 and we compute accurate upper and lower bounds to the Hartree energy for  $H^-$  and He.

PACS numbers: 31.10. + z

## I. INTRODUCTION

It is well known<sup>1-4</sup> that  $H^-$  has a single bound state of even spatial parity, i.e., the Hamiltonian (in reduced units)

$$H(Z) = -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (1.1)$$

has exactly one eigenvalue below  $-\frac{1}{2}$  when  $Z = 1$ . Although it is easy to produce trial functions which establish that  $H(1) < -\frac{1}{2}$ , we are not aware of any such functions which have the form of a single-determinant Hartree-Fock function. In this paper we show that, in fact, one cannot predict binding in  $H^-$  by using a spin-restricted form of the Hartree-Fock approximation which, for two electrons, is equivalent to the Hartree approximation.

Because confusion regarding terminology exists in the literature, we find it prudent to review some elementary definitions, so that we can state our results unambiguously. In the Hartree-Fock (HF) approximation, the exact ground state function  $\Psi$  for an  $N$ -particle Hamiltonian  $H_N$  is replaced by a trial function  $\Psi_{\text{HF}}$  consisting of a single Slater determinant, i.e., an antisymmetrized product of  $N$  single-particle functions,  $\{\phi_j\}_{j=1}^N$ . The Hartree-Fock energy is then given by

$$E_{\text{HF}} = \inf_{\Psi_{\text{HF}}} \frac{\langle \Psi_{\text{HF}} | H_N | \Psi_{\text{HF}} \rangle}{\langle \Psi_{\text{HF}} | \Psi_{\text{HF}} \rangle}, \quad (1.2)$$

which leads to a set of equations for  $\{\phi_j\}$ . In practice, the minimization in (1.2) is carried out using only a finite and restricted set of  $\{\phi_j\}$ . One common restriction, particularly when  $N = 2n$  is even, which we shall call the spin-restricted HF (SRHF) approximation, is to require that

$$\phi_{2k-1} = u_k(\mathbf{r})\alpha; \quad \phi_{2k} = u_k(\mathbf{r})\beta \quad (1.3)$$

(where  $\alpha, \beta$  are the usual spin eigenfunctions) and to choose  $\{u_j\}_{j=1}^n$  so as to minimize (1.2). If  $N = 2$ ,  $\Psi_{\text{SRHF}}$  has the exceedingly simple form  $(\alpha\beta - \beta\alpha) \times u(\mathbf{r}_1)u(\mathbf{r}_2)$ . The equation for  $u$  obtained from minimizing (1.2) is equivalent to that obtained from the so-called Hartree approximation, which we discuss below. Therefore, our results on the Hartree approximation for two-electron Hamiltonians of the form (1.1), also apply to the SRHF approximation.

In principle, no restrictions on the  $\{\phi_j\}$  are necessary. Indeed  $\phi_j$  need not even have the form (space function)

$\times$  (spin function), but could conceivably be something like  $\phi_j = f_j(r)\alpha + g_j(r)\beta$ . When the restrictions (1.3) are dropped, one sometimes emphasizes this by applying the term unrestricted HF (UHF) approximation. For two electrons one can make  $E_{\text{UHF}}(Z)$  arbitrarily close to  $-\frac{1}{2}Z^2$  by choosing  $\phi_1 = f_1(r)\alpha; \phi_2 = f_2(r)\beta$ , where  $f_k$  is any hydrogenic function satisfying  $(-\frac{1}{2}\Delta - Z/r)f_k = -(Z^2/2k^2)f_k$ , and making  $n$  large. Therefore, either the UHF approximation predicts binding for  $H^-$  or  $E_{\text{UHF}} = -\frac{1}{2}$  exactly. No approximate lower bound procedure can prove absence of binding for  $H^-$  in the UHF approximation. However, we know of no trial function which actually demonstrates that  $E_{\text{UHF}}(1) < -\frac{1}{2}$ .

Because single determinants, particularly those which minimize (1.2), need not be eigenfunctions of spin or orbital angular momentum operators, the HF approximation is sometimes generalized<sup>5</sup> to allow  $\Psi$  to be a linear combination of the minimal number of Slater determinants needed to make  $\Psi$  an eigenfunction of some specified set of angular momentum operators. An example for two electrons is the function

$$\Psi = [f(\mathbf{r}_1)g(\mathbf{r}_2) + g(\mathbf{r}_1)f(\mathbf{r}_2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)].$$

It has been shown that functions of this form do predict binding in  $H^-$ .<sup>4,6</sup> If one takes  $f = e^{-ar}$ ,  $g = e^{-br}$  with  $a = 1.03925$ ,  $b = 0.2831$  one finds that  $H(1) \leq -0.5133 < -0.5$ . Although this "spatial permanent" is reminiscent of a HF function, the  $f$  and  $g$  do not satisfy the HF equations and  $\Psi$  is not a single Slater determinant; it is actually a linear combination of two Slater determinants, one from  $\phi_1 = f(r)\alpha, \phi_2 = g(r)\beta$  and the other from  $\phi_3 = g(r)\alpha, \phi_4 = f(r)\beta$ .

In this paper we study the Hartree, or equivalently the SRHF, approximation for two-electron Hamiltonians of the form (1.1). The Hartree energy is given by

$$E_{\text{H}}(Z) = 2 \inf_{\|u\|=1} \Phi(u), \quad (1.4)$$

where

$$\Phi(u) = \frac{1}{2} \int |\nabla u|^2 d^3r - Z \int \frac{|u|^2}{r} d^3r + \frac{1}{2} \iint \frac{u^2(\mathbf{r})u^2(\mathbf{s})}{|\mathbf{r}-\mathbf{s}|} d^3r d^3s. \quad (1.5)$$

It is well-known that the continuous spectrum for  $H(Z) = [-Z^2/2, \infty)$  (see Ref. 7). We will say that the Hartree approximation predicts binding if  $E_{\text{H}}(Z) < -Z^2/2$ . We

<sup>a)</sup> On leave from Department of Mathematics, University of Lowell, Lowell, MA 01854. Present address: The Bunting Institute, Radcliffe College, Cambridge, MA 02138.

will show that the Hartree approximation does not predict binding for  $H^-$  or for any  $H(Z)$  with  $Z \leq 1.0268$ . We define  $Z_H$  by  $E_H(Z_H) = -Z_H^2/2$  and show that

$$1.0268 < Z_H < 1.0312.$$

The analogous quantity for the exact ground state energy,  $E_0(Z)$  of  $H(Z)$  is defined by  $-Z_C^2/2 = -E_0(Z_C)$ . Stillinger<sup>6,8</sup> calculated  $Z_C \approx 0.9112$ . Both the exact and the Hartree problems have the unusual feature that they have solutions at the crossing point, i.e.,  $H(Z)$  does have a square-integrable ground state for  $Z = Z_C$ ,<sup>9</sup> and (1.5) has a minimizing  $u$  for  $Z = Z_H$ .<sup>10</sup>

The question of whether or not the infimum in (1.4) is actually a minimum has been studied extensively.<sup>10-17</sup> By making the transformation

$$\rho(x) = [u(x/Z)/Z^2]^2,$$

one can consider the Hartree functional  $\Phi(u)$  to be a special case of the Thomas-Fermi-von Weizsäcker (TFW) functional for which the constant  $\gamma$  is 0 in the term  $\gamma \int \rho^{5/3} = \gamma \int u^{10/3}$ . Then one can use results of Benguria and Lieb<sup>18,19</sup> to show that there is a  $Z_M$  satisfying (1) for  $Z < Z_M$ , (1.4) has no minimizing  $u$  and  $E_H(Z) = -Z^3 A$  for some  $A > 0$ ; (2) for  $Z \geq Z_M$ , (1.4) has a minimizing  $u$  and  $E_H(Z) \geq -Z^3 A$  with equality only for  $Z = Z_M$ ; and (3)  $1/2 < Z_M < 1$ . Recently Baumgartner<sup>20</sup> has shown that  $Z_M \approx 0.828$ . It is interesting to note that, since  $Z_M < 1 < 1.0268 < Z_H$ , there is a nontrivial range of  $Z$ , i.e.,  $(Z_M, Z_H)$ , within which the Hartree functional  $\Phi(u)$  has a minimizing  $u$  yet the Hartree energy lies in the continuum for  $H(Z)$ . The region  $(Z_M, Z_H)$  includes the physically interesting case of  $H^-$  for which  $Z = 1$ .

Figure 1 schematically indicates the behavior of the energy curves  $E_0(Z)$  and  $E_H(Z)$ , with approximate placement of the distinguished points  $Z_M$ ,  $Z_C$ , and  $Z_H$ .

We compute lower bounds to both  $E_H(Z)$  and  $Z_H$  by using a modification of the Bazley and Seydel method<sup>21</sup> as described in Sec. II. Excellent upper bounds to both  $E_H(Z)$

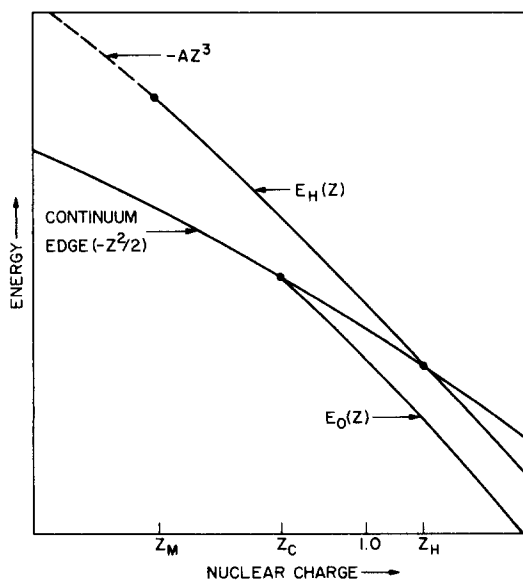


FIG. 1. Schematic diagram of  $Z$ -dependent energies for the two-electron problem.

and  $Z_H$  were obtained by approximating the Hartree trial function  $u$  by a linear combination of simple exponentials; this is discussed in Sec. III. In Sec. IV, we summarize our results for  $H^-$  ( $Z = 1$ ) and  $He$  ( $Z = 2$ ) which are generally better than results reported previously in the literature.

## II. LOWER BOUNDS

To obtain a lower bound to  $E_H(Z)$ , we use the method of Bazley and Seydel<sup>21</sup> which is based upon the inequality

$$\begin{aligned} & \iint \frac{u^2(\mathbf{r})u^2(\mathbf{s})}{|\mathbf{r}-\mathbf{s}|} d^3r d^3s \\ & \geq 2 \iint \frac{u^2(\mathbf{r})w^2(\mathbf{s})}{|\mathbf{r}-\mathbf{s}|} d^3r d^3s - \iint \frac{w^2(\mathbf{r})w^2(\mathbf{s})}{|\mathbf{r}-\mathbf{s}|} d^3r d^3s. \end{aligned} \quad (2.1)$$

Substituting (2.1) into (1.5) one finds

$$\Phi(u) \geq k_w u - \frac{1}{2} \iint \frac{w^2(\mathbf{r})w^2(\mathbf{s})}{|\mathbf{r}-\mathbf{s}|} d^3r d^3s, \quad (2.2)$$

where

$$k_w = -\frac{1}{2} \Delta - Z/r + q_w(r), \quad (2.3)$$

and

$$q_w(r) = \int \frac{w^2(\mathbf{s})}{|\mathbf{r}-\mathbf{s}|} d^3s. \quad (2.4)$$

Then

$$E_H(Z) \geq 2\lambda - \iint \frac{w^2(\mathbf{r})w^2(\mathbf{s})}{|\mathbf{r}-\mathbf{s}|} d^3r d^3s, \quad (2.5)$$

where  $\lambda$  is a lower bound to  $k_w$ . In previous applications of the Bazley-Seydel method,<sup>22</sup> attention was restricted to  $w$  for which  $q_w$  could be calculated from  $w$  by doing the integration in (2.4) exactly, after which one was still faced with the problem of finding a good lower bound to  $k_w$ .

Therefore, instead of selecting a trial  $w$ , we will choose  $q_w$  so that the lowest eigenvalue to  $k_w$  can be determined exactly; this eigenvalue will then serve as our lower bound  $\lambda$  in (2.5). We then use the electrostatic equality

$$\iint \frac{w^2(\mathbf{r})w^2(\mathbf{s})}{|\mathbf{r}-\mathbf{s}|} d^3r d^3s = \frac{1}{4\pi} \int |\nabla q_w|^2 d^3r$$

to conclude that

$$E_H(Z) \geq 2\lambda - \frac{1}{4\pi} \int |\nabla q_w|^2 d^3r. \quad (2.6)$$

We now choose  $q_w$  as follows. Let

$$u = \sum_{k=1}^N A_k e^{-a_k r}, \quad (2.7)$$

where  $A_k > 0$ ,  $a_{k+1} > a_k > 0$ , and

$$\sum_k A_k (Z - a_k) = 0. \quad (2.8)$$

Let

$$\begin{aligned} q_w(r) = & \frac{Z}{r} + \frac{1}{u} \left( \sum_{k=1}^{N-1} \frac{a_k^2 - a_N^2}{2} A_k e^{-a_k r} \right. \\ & \left. - \frac{1}{r} \sum_{k=1}^N a_k A_k e^{-a_k r} \right). \end{aligned} \quad (2.9)$$

Then  $k_w u = \lambda u$  with  $\lambda = -a_N^2/2$ . The constraint  $A_k > 0$  insures<sup>23</sup> that  $u(r)$  is strictly positive so that  $\lambda$  is the lowest eigenvalue of  $k_w$ , and  $q_w$  has no singularities, except possibly at  $r = 0$ . Condition (2.8) guarantees that  $u$  satisfies the nuclear cusp condition<sup>24</sup> and consequently that  $q_w$  has no pole at  $r = 0$ . Although we need not compute  $w$  explicitly, it can be verified that  $w = \sqrt{-\Delta q_w}$  is square-integrable, so that  $q_w$  can be obtained from an acceptable Hartree trial function. Since  $q_w$  is spherically symmetric,

$$E_H(Z) \geq -a_N^2 - \int_0^\infty r^2 |q'_w(r)|^2 dr. \quad (2.10)$$

If one now makes the substitutions

$$r = y/\epsilon Z, \\ a_k = Z(1 - \gamma_k \epsilon) \quad (k = 1 \dots N),$$

and lets  $\gamma_1 = -1$  so that  $a_1 = Z(1 + \epsilon)$  defines  $\epsilon$ , one finds

$$q_w(r) = \epsilon Z^2 \hat{q}_w(y) \\ = \frac{\epsilon Z^2}{\hat{u}(y)} \sum_k \left( \frac{\epsilon(\gamma_k^2 - \gamma_N^2)}{2} - (\gamma_k - \gamma_N) + \frac{\epsilon}{y} \gamma_k \right) A_k e^{\gamma_k y} \\ = \frac{\epsilon Z^2}{\hat{u}} \left( \frac{\epsilon \hat{u}''}{2} - \hat{u}' + \frac{\epsilon}{y} \hat{u}' \right) + \text{const},$$

where  $\hat{u}(y) = \sum_k A_k e^{\gamma_k y}$ . Then

$$\int_0^\infty r^2 |q'_w(r)|^2 dr = \epsilon Z^3 \int_0^\infty \frac{1}{\hat{u}^4(y)} [\epsilon S(y) + y T(y)]^2 dy, \quad (2.11)$$

where

$$T(y) = (\hat{u}')^2 - \hat{u} \hat{u}'' \\ = \sum_k \sum_l A_k A_l (\gamma_k \gamma_l - \gamma_l^2) e^{(\gamma_k + \gamma_l) y},$$

and

$$S(y) + T(y) = \frac{y}{2} (\hat{u} \hat{u}''' - \hat{u}' \hat{u}'') - \frac{\hat{u} \hat{u}'}{y} \\ = \sum_k \sum_l A_k A_l \left( \frac{\gamma_l^2 y}{2} (\gamma_l - \gamma_k) - \frac{\gamma_l}{y} \right) e^{(\gamma_k + \gamma_l) y}.$$

Thus  $E_H(Z) \geq F(Z)$ , where

$$F(Z) = -(1 - \gamma_N \epsilon)^2 Z^2 - \epsilon Z^3 (A \epsilon^2 + B \epsilon + C), \\ A = \int_0^\infty \left( \frac{S(y)}{\hat{u}^2(y)} \right)^2 dy, \\ B = \int_0^\infty \frac{y S(y) T(y)}{\hat{u}^4(y)} dy, \\ C = \int_0^\infty \left( \frac{y T(y)}{\hat{u}^2(y)} \right)^2 dy. \quad (2.12)$$

The quantity  $F(Z)$  gives a lower bound to  $E_H(Z)$  for all choices of  $A_1 \dots A_{N-1}$ ,  $\epsilon$ , and  $\gamma_2 \dots \gamma_N$ . [Here  $A_N$  is determined by (2.8) and  $\gamma_1 = 1$ .] Since  $F(Z)$  is independent of normalization, we can set  $A_1 = 1$  without loss of generality. We now search for values of the remaining parameters which optimize  $F(Z)$ . For each fixed choice of  $A_2 \dots A_{N-1}$ , and  $\gamma_2 \dots \gamma_{N-1}$ , the optimal  $\epsilon$  must satisfy

$$-2\gamma_N + 2\gamma_N^2 \epsilon + Z(3A\epsilon^2 + 2B\epsilon + C) = 0. \quad (2.13)$$

It can be shown that only one of the roots of (2.13) is positive

and this positive root maximizes  $F(Z)$ . A simple linear variation of  $A_2 \dots A_{N-1}$  and  $\gamma_2 \dots \gamma_{N-1}$  can then be used to maximize  $F(Z)$  to obtain the best possible lower bound of the form (2.7) for fixed  $N$  and  $Z$ .

Although one could bound  $Z_H$  by comparing  $F(Z)$  with  $-Z^2/2$ , we used the following direct approach. Suppose  $F(\tilde{Z}) = -\tilde{Z}^2/2$  then  $E_H(\tilde{Z}) \geq -\tilde{Z}^2/2$ , which implies  $\tilde{Z} < Z_H$ . To find  $\tilde{Z}$  we note that

$$+\frac{1}{2} - (1 - \gamma_N \epsilon)^2 = \tilde{Z} \epsilon (A \epsilon^2 + B \epsilon + C). \quad (2.14)$$

One can eliminate  $\tilde{Z}$  from (2.13) and (2.14) to see that the optimal  $\epsilon$  for  $\tilde{Z}$  must satisfy the quartic equation

$$\gamma_N^2 A \epsilon^4 - 4\gamma_N A \epsilon^3 \\ + (3A/2 - 2\gamma_N B - \gamma_N^2 C) \epsilon^2 + B \epsilon + C/2 = 0. \quad (2.15)$$

Although (2.15) can have four roots, we found that, in practice, it has only one real root in the acceptable range  $1 > \gamma_N \epsilon > 1 - 1/\sqrt{2} > 0.29$  [where the second inequality follows from the condition  $-Z^2/2 < F(Z) < -(1 - \gamma_N \epsilon) Z^2$ ]. Once  $\epsilon$  is fixed,  $\tilde{Z}$  can be found from either (2.13) or (2.14). A simple variation of  $A_2 \dots A_{N-1}$  and  $\gamma_2 \dots \gamma_{N-1}$  can then be used to maximize  $\tilde{Z}$ .

Our results are summarized in Table I. Three exponentials suffice to show that  $Z_H > 1.0$  which implies that the Hartree approximation cannot predict binding in  $H^-$ . Four exponentials give  $Z_H > 1.02683$  which is remarkably close to the upper bound (next section) of 1.031 18. In calculating  $\tilde{Z}$ , no attempt was made to estimate numerical errors during the variation process itself. Instead, a double precision lower bound was computed for  $E_H$  (1.026 831) with careful error estimates. These results, namely  $E_H > -0.527 190 945 > -0.527 190 951 = -(1.026 831)^2/2$ , verify that  $Z_H > 1.026 831$  is indeed a valid bound.

### III. UPPER BOUNDS

To obtain upper bounds to  $E_H$ , we again approximate  $u$  by a finite linear combination of exponentials. Thus  $E_H \leq 2\Phi(u)$  with  $u$  given by (2.7) except that the  $A_k$  are required to satisfy the normalization condition,  $\sum_k \sum_l A_k A_l / (a_k + a_l)^3 = 1$ , rather than the cusp condition (2.8). If we make the substitutions  $t = a_1 r$ ,  $a_j = \gamma_j a_1$  ( $j = 1 \dots N$ ) and let  $a$  denote  $a_1$ , then  $2\Phi(u)$  can be written in the form

$$2\Phi(u) = G(a, Z) = a^2 P - 2aZQ + aR. \quad (3.1)$$

Here  $P$ ,  $Q$ , and  $R$  are elementary integrals of exponentials which can be evaluated exactly as algebraic combinations of the  $A_k$ 's and  $\gamma_k$ 's. For fixed  $Z$ ,  $G(a, Z)$  has its minimum at  $a = (ZQ - R/2)/P$ , so that

$$E_H \leq G(a_{\min}, Z) \\ = -(ZQ - R/2)^2/P. \quad (3.2)$$

A linear variation of  $A_2 \dots A_N$ , and  $\gamma_2 \dots \gamma_N$  was used to optimize (3.2). Results are summarized in Table II. The quantity  $C = \sum_k a_k A_k / (Z \sum_k A_k)$  was calculated as a measure of how closely the cusp condition (2.8) was satisfied.

An upper bound,  $Z_H^u$ , to  $Z_H$  can be obtained from the condition

$$-(Z_H^u)^2/2 = -(Z_H^u Q - R/2)^2/P. \quad (3.3)$$

This has solutions

TABLE I. Bounds on  $Z_H$ .

$N$	Type	$Z_H$	$E_H(Z_H)$	Cusp
1	up	1.066 942	-0.569 182	0.707
1 <sup>a</sup>	lo	0.0	0.0	1.0
2	up	1.031 403	-0.531 896	0.970
2	lo	0.951 550	-0.452 724	1.0
3	up	1.031 178	-0.531 664	1.006
3	lo	1.016 472	-0.516 608	1.0
4	up	1.031 178	-0.531 664	1.008
4	lo	1.026 831	-0.527 191	1.0

<sup>a</sup>Lower bounds with  $N = 1$  are included here and in Tables II and IV for comparison purposes only. The methods of Sec. II are not strictly valid, since formal application of (2.7) to (2.10) implies  $w = 0$  when  $N = 1$ .

$$Z_H^u = R / (2Q \mp \sqrt{2P}).$$

However, the smaller solution gives a negative expression for  $a_{\min}$  which corresponds to a non-square-integrable  $u$ . Therefore, we conclude that

$$Z_H \leq R / (2Q + \sqrt{2P}).$$

Our results are summarized in Table I. A single exponential has no parameters except  $a$  and gives the remarkably good result  $Z_H < \frac{2}{3}(1 + 1/\sqrt{2}) < 1.067$ . This approximation to  $Z_H$  was then used as the first value of  $Z$  in the cycle of two-exponential calculations, and the predicted value for  $Z_H$  was used for each subsequent variation. This procedure rapidly converged to the bound  $Z_H < 1.031 178$ . When combined with our previous lower bound results, we can state with confidence that  $Z_H = 1.03$  to three significant figures and  $1.0268 \leq Z_H < 1.0312$ .

#### IV. H<sup>-</sup> AND He

Upper and lower bounds on the Hartree energy for H<sup>-</sup> ( $Z = 1$ ), and He ( $Z = 2$ ), were carried out using the procedures described in Secs. II and III. The results are summarized in Table II. We find  $-0.489 651 \leq E_H(1) \leq -0.487 929$

TABLE II. Bounds on Hartree energy for H<sup>-</sup> and He.

$Z$	$N$	Type	Energy	Cusp	$\ u_{\text{up}} - u_{\text{lo}}\ $	Overlap
1.0	1	up	-0.472 656	0.687		
1.0	1	lo	-1.0	1.0	0.3194	0.949 003
1.0	2	up	-0.487 824	0.966		
1.0	2	lo	-0.517 203	1.0	0.0759	0.997 116
1.0	3	up	-0.487 929 3	1.005		
1.0	3	lo	-0.493 691	1.0	0.0213	0.999 773
1.0	4	up	-0.487 929 6	1.007		
1.0	4	lo	-0.489 651	1.0	0.0067	0.999 978
2.0	1	up	-2.847 656	0.375		
2.0	1	lo	-4.0	1.0	0.1467	0.989 246
2.0	2	up	-2.861 672	1.002		
2.0	2	lo	-2.904 016	1.0	0.0130	0.999 915
2.0	3	up	-2.861 679	1.006		
2.0	3	lo	-2.870 400	1.0	0.0027	0.999 996
2.0	4	up	-2.861 679			
2.0	4	lo	-2.864 674	1.0	0.0007	0.999 999 7

for H<sup>-</sup>, and  $-2.864 674 \leq E_H(2) \leq -2.861 679$  for He.

When compared with previously published bounds, these results are quite gratifying. The difference between the upper and lower bounds for both H<sup>-</sup> and He is less than 0.003. We attribute this agreement to the unusually good lower bounds we obtain by circumventing the need to find first a lower bound to  $k_w$ , which was constructed instead to be exactly solvable. Our lower bound for He represents an improvement of over 0.018 from the value of  $-2.882 356$  reported by Behling *et al.*<sup>22</sup> We are surprised at the apparent accuracy of upper bounds obtained from a simple linear combination of exponentials. Using only three exponentials we were able to obtain a better upper bound on the Hartree energy for H<sup>-</sup> than Froese-Fischer<sup>25</sup> obtained using a linear combination of 11 hydrogenic orbitals. Our upper bound for He is also in remarkably close ( $10^{-6}$ ) agreement to that reported by Froese-Fischer.<sup>25</sup> A comparison of our bounds to those reported previously is summarized in Table III.

A few comments about the optimizing functions are in order. A list of parameters for the various optimizing functions is given in Table IV. Although the optimal coefficients for the upper and lower bound functions for fixed  $Z$  and given  $N$  seem rather different, plots of the actual functions indicate that they are pointwise quite close, at least for  $N = 4$ . A comparison of the norm of the difference between the upper- and lower-bound functions shows that they are very close for  $N \geq 3$ . When comparing the upper- and lower-bound functions, it should be kept in mind that one is doing an apples versus oranges type of comparison. The upper bound function is an approximation to the function which minimizes (1.5) and therefore solves the Hartree eigenvalue problem; the lower bound function solves a different, but related, eigenvalue problem, namely  $k_w u = (a_N^2/2)u$ . However, since both approximations can be expected to converge to the exact Hartree minimizing function, the observed agreement is to be expected.

Our variational procedure found the energy surface to be quite flat; substantial changes in the variation parameters produced insignificant changes in the energy. We attribute this primarily to the fact that first-order changes in the parameters will, in general, produce second- or higher-order

TABLE III. Comparison with other energy bounds.

	$Z = 1$	$Z = 2$
Hartree upper bounds		
3-exponential	-0.487 929 3	-2.861 679
4-exponential	-0.487 929 6	-2.861 679
Froese-Fischer <sup>a</sup>	-0.487 927	-2.861 680
Behling <i>et al.</i> <sup>b</sup>	...	-2.861 58
Hartree lower bounds		
3-exponential	-0.493 691	-2.870 400
4-exponential	-0.489 651	-2.864 674
Behling <i>et al.</i> <sup>b</sup>	...	-2.882 356
Precise correlated (not HF)		
Pekeris <sup>c</sup>	-0.527 751	-2.903 724

<sup>a</sup>Reference 25.

<sup>b</sup>Reference 22.

<sup>c</sup>Reference 3.

TABLE IV. Summary of optimizing parameters.

Z	N	Type	Unnormalized coefficients				Exponents				
			A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>	a <sub>4</sub>	
1.069 9	1	up	1.0				0.687 5 <sup>a</sup>				
0.0	1	lo	1.0				1.0 <sup>b</sup>				
1.031 403	2	up	1.0	0.529 438			1.268 812	0.493 360			
0.951 550	2	lo	1.0	0.368 683			1.165 260	0.371 892			
1.031 178	3	up	1.0	1.052 094	0.421 745		1.555 878	0.793 467	0.413 478		
1.016 472	3	lo	1.0	0.652 611	0.160 813		1.384 725	0.617 704	0.344 805		
1.031 178	4	up	1.0	3.384 017	3.415 354	1.392 050	1.879 396	1.358 213	0.736 340	0.404 855	
1.026 831	4	lo	1.0	0.779 303	0.242 388	0.068 309	1.460 684	0.717 123	0.418 579	0.342 300	
1.0	2	up	1.0	0.492 644			1.214 425	0.462 200			
1.0	2	lo	1.0	0.401 462			1.235 018	0.414 595			
1.0	3	up	1.0	1.034 584	0.374 117		1.499 283	0.753 114	0.380 748		
1.0	3	lo	1.0	0.650 161	0.149 785		1.360 014	0.601 520	0.326 114		
1.0	4	up	1.0	1.117 301	0.508 448	0.164 404	1.556 349	0.853 731	0.481 322	0.333 077	
1.0	4	lo	1.0	0.780 810	0.228 671	0.055 143	1.419 772	0.689 600	0.390 293	0.311 147	
2.0	2	up	1.0	1.640 902			2.906 239	1.452 963			
2.0	2	lo	1.0	1.224 015			2.747 452	1.389 344			
2.0	3	up	1.0	0.730 100	1.419 830		3.074 542	1.307 938	1.627 090		
2.0	3	lo	1.0	0.774 050	0.988 864		2.917 102	1.630 428	1.361 859		
2.0	4	up	1.0	0.299 382	0.875 678	1.071 215	3.095 529	1.705 568	1.696 055	1.347 738	
2.0	4	lo	1.0	0.761 538	0.544 252	0.740 025	2.988 910	1.744 292	1.415 324	1.356 822	

<sup>a</sup> = Z - 1/2.

<sup>b</sup> = Z.

changes in the energy. The parameters we report should probably be regarded as sufficient to prove our results rather than optimal. It is curious to note that the cusp factor worsens rather than improves as one increases the number of exponentials. Presumably this illustrates the principle that one expects to obtain a lower approximating energy if one does not impose unnecessary constraints on approximating functions, even when the exact solution is known to satisfy these constraints.

**ACKNOWLEDGMENTS**

One of us (MBR) is grateful to Professor N. Bazley for arranging a visit to the University of Cologne at which time Ref. 21 was brought to her attention.

All calculations were carried out on a Cray-1 computer, using the numerical integration routines in the PORT FORTRAN library of Bell Laboratories.

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<sup>25</sup>See Ref. 5, p. 165.