which are the eigenvalues of the operators $\Gamma^{(2)}, L^2, S_z, \cdots$. Further the natural geminals, which are antisymmetric by definition, were seen in the functions analyzed here to have a general functional form that for the more important terms, those with eigenvalues which are relatively large, is not too sensitive to the degree of goodness of the wave function Ψ. For the Weiss functions the natural orbital representation of the natural geminals was seen to have the same general structure as for the functions over an orthogonal basis, as shown in Eqs. (45) and (46).

In discussing the natural geminal expansion we have left unanswered the question concerning the antisymmetric properties of the truncated expansion. This question is important however as the economy of form pointed out earlier for the Weiss function indicates. In all cases where $N=2p$ the sign of the natural expansion coefficients are uniquely determined by the original wave function since as shown the transformations diagonalizing $\Gamma(1,\cdots,p;1',\cdots,p')$ and $\Gamma(p+1,\cdots,N;(p+1)',\cdots,N')$ can be chosen to have the same phase.

The eigenvalue degeneracy problem was shown to be explainable simply in terms of the two-electron spin functions. The dependence of the degeneracy pattern on functional form of Ψ was explained in the same terms.

The results of our work have elucidated the structure of the 2-matrix in great detail. It is hoped that the result will bring the eventual solution of the N-representability of the 2-matrix a step closer. In the meantime we hope to find through further research that the natural geminals and the natural geminal expansion will give insight into the two-electron interactions within physical systems and provide a useful way of capitalizing on the chemist's concept of the two-electron chemical bond in describing molecular structure and chemical reactivity.

PHYSICAL REVIEW VOLUME 153, NUMBER 1 5 JANUARY 1967

Variational Lower Bounds on Electron Hydrogen *s*-Wave Phase Shifts*†

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(Received 15 July 1966)

The variational-bound (or minimum-principle) formulation for single-channel scattering was applied to the calculation of rigorous lower bounds on the *s*-wave phase shifts for the scattering of electrons by hydrogen atoms (e^-H) for energies below the excitation threshold. This method was previously applied to positron-hydrogen (e^+H) elastic scattering. Because of the exchange effect in the e^-H case, a projection operator is employed which projects out of the wave function those states in which either or both of the electrons are in the ground state. The method requires the exact solution of the static equation, and of the corresponding static Green's function G^P, which is expressed in terms of the solution of an integral equation. Trial functions are chosen which are spatially symmetrized (or antisymmetrized) and correspond to states of the hydrogen atom of given angular momentum quantum number l; the associated radial functions contain nonlinear variational parameters. The e^-H calculations are found to give much more accurate results for a given number of parameters than the e^+H calculations.

1. INTRODUCTION

A NUMBER of methods have been developed recently for the study of the scattering of one compound system by another.[1] These approaches are practical for relatively simple systems. From a strictly logical standpoint, the most satisfying approach, perhaps, is the variational-bound (VB) formulation.[2–4] (In earlier papers, it was called a minimum-principle formulation.) The VB formulation is the analog in the continuum energy region of the Rayleigh-Ritz principle and its extensions, which provide variational bounds on the discrete energy eigenvalues and a procedure for systematically improving these variational bounds. The VB method provides bounds on the parameters which characterize the scattering process.

As appealing as the VB method may be in principle,

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* The work reported on in this article was sponsored by the U. S. Office of Naval Research, the Advanced Research Projects Agency under Contract Nonr-285(49), NRO12-109, and NASA under Contract No. NSG 699.

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[1] (a) See, for example, P. G. Burke and K. Smith, Rev. Mod. Phys. **34**, 458 (1962); (b) also N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, England, 1965), 3rd ed., for a review of recent developments.

[2] L. Spruch and L. Rosenberg, Phys. Rev. **116**, 1034 (1959); L. Rosenberg, L. Spruch, and T. F. O'Malley, *ibid.* **118**, 184 (1960).

[3] Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **130**, 381 (1963).

[4] Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **134**, B911 (1964).

the question remains of the domain of its practical applicability. No difficulties arise at zero incident kinetic energy,[2] but at nonzero incident kinetic energies[3] the VB approach requires the numerical evaluation of the Green's function G^P associated with the static approximation equation and the subsequent (numerical) evaluation of various integrals involving G^P. The ease with which these evaluations can be performed is a measure of the utility of the VB approach.

The VB formulation has previously been used at nonzero incident kinetic energies for only one problem, the low-energy (elastic) scattering of positrons by hydrogen atoms (e^+H) where it yielded rigorous variational lower bounds on the phase shifts for $L=0$[5] and for $L=1$ and 2.[6] A comparison with reliable results was possible only for the $L=0$[7] and $L=1$[8] cases; the rigorous variational lower bounds were there found to be reasonably accurate.

We here apply the VB method to the much more interesting but also more difficult problem of elastic electron–atomic-hydrogen (e^-H) scattering. At low energies, where the distortion of the hydrogen atom is great enough to invalidate the Born approximation, other techniques[1] have been used for calculating the cross sections. These techniques make use of various approximations, the validities of which are difficult to establish. It is nevertheless reasonably certain that the $L=0$ singlet and triplet phase shifts that have been obtained[7] are quite accurate. Our purpose then, clearly, is not to obtain more accurate results but to test the efficacy of the VB approach for this more difficult problem. Since one can make the definitive statement about a VB result that it represents a (variational) bound, the kind of statement that cannot be made for any other method, it seems fair to say that the VB approach is superior to any other approach that requires comparable effort.

Sugar and Blankenbecler[9] have recently given a variational bound which appears to be different from the original version but which in fact is formally identical.[10] The still more recent formulation of Rosenberg[11] is not quite formally equivalent[10] to the original version.

2. THE VARIATIONAL-BOUND FORMULATION

In this section we formulate a method for obtaining variational lower bounds on the phase shifts for an arbitrary total orbital angular momentum L for (elastic) e^-H scattering at energies below the excitation threshold 10.2 eV. We neglect the spin-orbit interaction and take the Hamiltonian H to be

$$H=-(\hbar^2/2m)(\nabla_1^2+\nabla_2^2)-e^2(1/r_1+1/r_2-1/r_{12})\,, \quad (2.1)$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the incident electron and the bound electron relative to the proton, which we consider fixed, and r_{12} designates the interelectronic separation. Since the total spin angular momentum S is conserved, the triplet case $S=1$ and the singlet case $S=0$ can be treated separately. We can deal with wave functions $\Psi_S(\mathbf{r}_1,\mathbf{r}_2)$ which do not depend upon the spin coordinates, but which have the property that

$$\Psi_S(\mathbf{r}_1,\mathbf{r}_2)=\epsilon\Psi_S(\mathbf{r}_2,\mathbf{r}_1)\,, \quad (2.2)$$

where $\epsilon=+1$ for the singlet case and $\epsilon=-1$ for the triplet case. We expand $\Psi_S(\mathbf{r}_1,\mathbf{r}_2)$ as

$$\Psi_S(\mathbf{r}_1,\mathbf{r}_2)=\sum A_{LMS}\Psi_{LMS}(\mathbf{r}_1,\mathbf{r}_2)\,, \quad (2.3)$$

where M denotes the total orbital angular momentum projection. Since e^2/r_{12} does not mix states which differ in L or M, the Schrödinger equation can be written as

$$(H-E)\Psi_{LMS}(\mathbf{r}_1,\mathbf{r}_2)=0\,. \quad (2.4)$$

The total energy E is given by

$$E=E_{T0}+E'=-13.6\text{ eV}+\hbar^2k^2/2m\,,$$

where E_{T0} and E' represent the ground-state energy of the hydrogen atom and the energy of the incident electron, respectively. Since only the elastic channel is open, and since the scattering is independent of M, the scattering for fixed L and S, for all M, is characterized by a single parameter, the phase shift η_{LS}. We will often omit one or all of the subscripts L, M, and S. The phase shift η, modulo π, is determined by the asymptotic form of the regular solution of (2.4), given by

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)\to(1+\epsilon S_{12})R(r_1)\mathcal{Y}_{L0L}^M(\Omega_{12})\times\frac{\sin(kr_2-\frac{1}{2}L\pi+\eta)}{2^{1/2}r_2\sin(\eta-\theta)}\,, \quad r_1 \text{ or } r_2\to\infty\,, \quad (2.5)$$

where the exchange operator S_{12} interchanges the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$. The coordinates $\mathbf{r}_i$ are given by

$$\mathbf{r}_i=r_i,\theta_i,\varphi_i=r_i,\Omega_i\,,\quad i=1 \text{ or } 2\,, \quad (2.6)$$

where the angles refer to some arbitrary space-fixed axis. $R(r)$ differs from the normalized ground state wave function $\psi_{T0}(r)$ of the hydrogen atom only by a normalization constant. We have

$$R(r)=(4\pi)^{1/2}\psi_{T0}(r)=2a_0^{-3/2}\exp(-r/a_0)\,, \quad (2.7)$$

where a_0 is the Bohr radius. The vector spherical harmonic $\mathcal{Y}_{L0L}^M$ is defined by

$$\mathcal{Y}_{Ll_1l_2}^M(\Omega_{12})=\sum_{m_1,m_2}C_{l_1l_2}(L,M;m_1,m_2)\times Y_{l_1m_1}(\Omega_1)Y_{l_2m_2}(\Omega_2)\,, \quad (2.8)$$

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[5] Y. Hahn and L. Spruch, Phys. Rev. **140**, A18 (1965).

[6] C. J. Kleinman, Y. Hahn, and L. Spruch, Phys. Rev. **140**, A413 (1965).

[7] C. Schwartz, Phys. Rev. **124**, 1468 (1961); **126**, 1015 (1962), and other references to be discussed later.

[8] R. L. Armstead (private communication), and Bull. Am. Phys. Soc. **10**, 736 (1965).

[9] R. Sugar and R. Blankenbecler, Phys. Rev. **136**, B472 (1964).

[10] Y. Hahn and L. Spruch, Phys. Rev. (to be published). A mathematical identity shows the equivalence of the two formulations for a given trial function.

[11] L. Rosenberg, Phys. Rev. **138**, B1343 (1965).

where the $C_{l_1l_2}(L,M;m_1,m_2)$ are the Clebsch-Gordan coefficients. l_1 and l_2 are the orbital angular momenta of the two electrons, and m_1 and m_2 are the orbital angular momenta projections. The normalization constant θ is arbitrary.

The VB formulation requires the introduction of two projection operators, P and Q, such that QHQ has no continuous spectrum below the energy E. The projection operators required[12] are

$$P=P_1+P_2-P_1P_2 \tag{2.9}$$

and

$$Q=1-P, \tag{2.10}$$

where P_1 projects onto the ground state of the hydrogen atom in the space of the first electron, such that, for any function $F(\mathbf{r}_1,\mathbf{r}_2)$,

$$P_1F(\mathbf{r}_1,\mathbf{r}_2)=\psi_{T0}(r_1)\int d\mathbf{r}_1'\psi_{T0}(r_1')F(\mathbf{r}_1'.\mathbf{r}_2), \tag{2.11}$$

and P_2 is the corresponding operator in the space of the second electron. It is convenient to include in the operator P_i the angular coordinates of both electrons. It is easily shown that for functions of the form

$$F(\mathbf{r}_1,\mathbf{r}_2)=f(r_1,r_2)\mathcal{Y}_{Ll_1l_2}(\Omega_{12}), \tag{2.12}$$

Eq. (2.11) can be written as

$$P_1F(\mathbf{r}_1,\mathbf{r}_2)=R(r_1)\mathcal{Y}_{L0L}(\Omega_{12})\int r_1'^2dr_1'd\Omega_{12}'R(r_1')$$
$$\times\mathcal{Y}_{L0L}^*(\Omega_{12}')F(r_1',r_2,\Omega_{12}'), \tag{2.13}$$

where Ω_{12}' denotes θ_1', φ_1', θ_2', φ_2'.

The VB inequality with the subtraction terms deleted is given by[3]

$$(k\hbar^2/2m)[\cot(\eta-\theta)-\cot(\eta^P-\theta)]\leq 2(P\Psi^P,PHQ\Psi_t)$$
$$+(Q\Psi_t,Q[\mathcal{H}-E]Q\Psi_t). \tag{2.14}$$

$Q\Psi_t(\mathbf{r}_1,\mathbf{r}_2)$ is the trial function, which vanishes faster than $1/r_i^{3/2}$ as $r_i\rightarrow\infty$. $P\Psi^P$ is the regular solution of the static or no-polarization equation

$$P(H-E)P\Psi^P=0, \tag{2.15}$$

which has the form

$$P\Psi^P(\mathbf{r}_1,\mathbf{r}_2)=(1+\epsilon S_{12})R(r_1)\mathcal{Y}_{L0L}(\Omega_{12})$$
$$\times u^P(r_2)/(2^{1/2}r_2), \tag{2.16a}$$

where $u^P(r_2)$ is regular at the origin, and, as $r_2\rightarrow\infty$, has the asymptotic form

$$u^P(r_2)\rightarrow -kr_2[(\sin\eta^P)n_L(kr_2)-(\cos\eta^P)j_L(kr_2)]/$$
$$\sin(\eta^P-\theta). \tag{2.16b}$$

The j_L and n_L are spherical Bessel and spherical Neumann functions, respectively, and η^P is the static-approximation phase shift. Substituting (2.16a) into (2.15) and operating on the resulting equation with P_1, one obtains the integro-differential equation for $u^P(r_2)$,

$$D(r_2)u^P(r_2)+\epsilon\int_0^\infty dr_1W(r_1,r_2)u^P(r_1)=0, \tag{2.17}$$

where

$$D(r)\equiv\frac{\hbar^2}{2m}\left[\frac{-d^2}{dr^2}+\frac{L(L+1)}{r^2}+V_{00}(r)-k^2\right] \tag{2.18}$$

and

$$W(r_1,r_2)\equiv r_1R(r_1)r_2R(r_2)$$
$$\times\left[-(E-2E_{T0})\delta_{L0}+\frac{e^2}{2L+1}\frac{r_<^L}{r_>^{L+1}}\right], \tag{2.19}$$

where δ_{L0} is the Kronecker delta symbol. The static potential $(\hbar^2/2m)V_{00}$ is defined by

$$V_{00}(r_2)=\frac{2m}{\hbar^2}\int r_1^2dr_1d\Omega_{12}|R(r_1)\mathcal{Y}_{L0L}(\Omega_{12})|^2$$
$$\times\left[\frac{-e^2}{r_2}+\frac{e^2}{r_{12}}\right]$$
$$=\frac{-2}{a_0}\left(\frac{1}{a_0}+\frac{1}{r_2}\right)\exp\left(\frac{-2r_2}{a_0}\right), \tag{2.20}$$

and $r_<$ and $r_>$ are the smaller and larger, respectively, of r_1 and r_2. The static equation (2.17) can be solved numerically on a computer and η^P can thus be determined. The modified Hamiltonian $\mathcal{H}$ is defined by

$$\mathcal{H}\equiv Q[H+HPG^PPH]Q, \tag{2.21}$$

where G^P is the static Green's function defined by

$$G^P\equiv P[P(E-H)P]^{-1}P, \tag{2.22}$$

and the boundary conditions determined by the asymptotic form of $P\Psi$ and $P\Psi^P$ in the equation

$$P\Psi=P\Psi^P+G^PPHQ\Psi. \tag{2.23}$$

The Green's function G^P has the form[13]

$$G^P(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}_1',\mathbf{r}_2')=\sum\nolimits_\epsilon 2\times\tfrac{1}{2}(1+\epsilon S_{12})\times\tfrac{1}{2}(1+\epsilon S_{12}')$$
$$\times R(r_1)\mathcal{Y}_{L0L}(\Omega_{12})R(r_1')\mathcal{Y}_{L0L}^*(\Omega_{12}')$$
$$\times g(\epsilon;r_2,r_2')/(r_2r_2'), \tag{2.24}$$

where in the sum ϵ assumes the values $+1$ and -1, and where S_{12}' interchanges $\mathbf{r}_1'$ and $\mathbf{r}_2'$. Here $g(\epsilon;r_2,r_2')$

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[12] Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **128**, 932 (1962).

[13] I. Aronson, Y. Hahn, P. M. Henry, C. J. Kleinman, and L. Spruch (to be published) contains a complete discussion of the formal specification of G^P and of the procedures that enable one to numerically determine G^P.

is the solution of the equation

$$g(\epsilon;\, r_2,r_2')=g_0(r_2,r_2')+\epsilon\int dt\, g_0(r_2,t)\int ds\, W(t,s)g(\epsilon;\, s,r_2')$$
$$+\delta_{L0}\delta_{-1\epsilon}\int dt\, g_0(r_2,t)tR(t)r_2'R(r_2'), \quad (2.25)$$

where

$$g_0(r_2,r_2')=-\frac{2m}{\hbar^2k}\{u_{\text{reg}}{}^D(r_<)u_{\text{irreg}}{}^D(r_>)$$
$$-[\cot(\eta^D-\theta)]u_{\text{reg}}{}^D(r_<)u_{\text{reg}}{}^D(r_>)\}. \quad (2.26)$$

Here $u_{\text{reg}}{}^D$ and $u_{\text{irreg}}{}^D$ are the regular and irregular solutions of the equation

$$D(r_2)u^D(r_2)=0, \quad (2.27)$$

with the asymptotic forms, as $r_2\to\infty$, given by

$$u_{\text{reg}}{}^D(r_2)\to -kr_2[n_L(kr_2)-\cot(\eta^D)j_L(kr_2)]\sin\eta^D$$
$$u_{\text{irreg}}{}^D(r_2)\to -kr_2[j_L(kr_2)$$
$$-\cot(\eta^D)n_L(kr_2)]\sin\eta^D. \quad (2.28)$$

The phase shift η^D is defined by (2.27) and (2.28).

We write the trial function $Q\Psi_t(\mathbf{r}_1,\mathbf{r}_2)$ in terms of the set of coordinates r_1, r_2, Ω_{12} rather than the set of coordinates involving r_1, r_2, r_{12}, and three Eulerian angles. The advantages and disadvantages of using the former set have been discussed in Refs 5. and 6. We expand the trial function for the two electrons in terms of one-particle functions each of which corresponds to an electron in a definite orbital angular momentum state l. This differs from the close-coupling approach, where the trial function is expanded in states of both definite orbital angular momentum l and principal quantum number n of the target. The advantage of our expansion is that we thereby include the effect of many eigenstates of the target with different values of n, including continuum eigenstates. We note that for $L>0$ and for $l_1>0$ more than one value of l_2 is allowed by the usual vector addition rule

$$|L-l_1|\leq l_2\leq L+l_1, \quad (2.29\text{a})$$

subject to the parity conservation rule

$$(-1)^{l_1+l_2-L}=1. \quad (2.29\text{b})$$

We impose the restriction that

$$l_2\geq l_1, \quad (2.29\text{c})$$

to avoid duplication of terms in the trial function, and designate a pair of values of l_1 and l_2 by γ. We take a trial function of the form

$$Q\Psi_t(r_1,r_2,\Omega_{12})=(1+\epsilon S_{12})\sum_{\gamma,i}c_{\gamma i}w(l_1,b_{\gamma i};\, r_1/a_0)$$
$$\times w(l_2,d_{\gamma i};\, r_2/a_0)\mathcal{Y}_{Ll_1l_2}(\Omega_{12})/(r_1r_2a_0{}^{1/2})$$
$$\equiv\sum_q c_qQ\Psi_{tq}. \quad (2.30)$$

For any fixed L, the index i varies from zero up to some arbitrary value which depends on γ; in the last form, we let the index q stand for both γ and i. The c's are linear variational parameters while the b's and the d's are nonlinear variational parameters. The function w must satisfy the conditions

$$w(l,t;\, x)\to x^{l+1}, \quad x\to 0 \quad (2.31\text{a})$$

and

$$x^{1/2}w(l,t;\, x)\to 0, \quad x\to\infty. \quad (2.31\text{b})$$

We choose for w the form

$$w(l,t;\, x)=x^{l+1}e^{-tx}-8(1+t)^{-3}xe^{-x}\delta_{0l}. \quad (2.32)$$

The distinction between $l=0$ and $l\neq 0$ is a consequence of the fact that for $l\neq 0$ the orthogonality to ψ_{T0} is automatically accomplished by the presence of the $\mathcal{Y}_{Ll_1l_2}$, while for $l=0$ one must choose the radial function to be orthogonal to ψ_{T0}.

We introduce the quantities

$$N_q\equiv(2ma_0/\hbar^2)(P\Psi^P,PHQ\Psi_{tq}) \quad (2.33)$$

and

$$K_{qq'}\equiv(2ma_0/\hbar^2)(Q\Psi_{tq},Q[\mathcal{H}-E]Q\Psi_{tq'}), \quad (2.34)$$

where q' represents γ' and i'. Equation (2.14) can then be written as

$$ka_0[\cot(\eta-\theta)-\cot(\eta^P-\theta)]\leq\Delta_\theta, \quad (2.35)$$

where Δ_θ is defined as

$$\Delta_\theta\equiv 2\sum_q c_qN_q+\sum_{qq'}c_qK_{qq'}c_{q'}, \quad (2.36)$$

or, more compactly,

$$\Delta_\theta=2\mathbf{C}^T\mathbf{N}+\mathbf{C}^T\mathbf{K}\mathbf{C}, \quad (2.37)$$

where $\mathbf{C}$ and $\mathbf{N}$ are vectors and $\mathbf{K}$ is a symmetric matrix whose dimension is equal to the number of terms included in $Q\Psi_t$.

For a given choice of the nonlinear parameters, $\mathbf{C}$ is determined by minimizing the right-hand side of (2.37). We obtain

$$\mathbf{C}=-\mathbf{K}^{-1}\mathbf{N}, \quad (2.38)$$

so that

$$\Delta_\theta=-\mathbf{N}^T\mathbf{K}^{-1}\mathbf{N}=\mathbf{N}^T\mathbf{C}. \quad (2.39)$$

Note that Δ_θ is independent of the normalization of the trial function $Q\Psi_t$, which enters quadratically in the numerator and in the denominator in (2.39). If we choose $\theta=\frac{1}{2}\pi+\eta^P$, the inequality given by (2.35) reduces to the simple form

$$ka_0\tan(\eta-\eta^P)\geq-\Delta, \quad (2.40)$$

where Δ represents Δ_θ for $\theta=\frac{1}{2}\pi+\eta^P$.

3. RESULTS AND DISCUSSION

In order to check the computer program, we first obtained a bound on the $L=0$ phase shift for the case when the target is allowed to be virtually excited to

TABLE I. The $L=0$ phase shifts in radians in various approximations. The 1s or static phase shifts were obtained by iterative techniques. CCA, VB, Mod VB, Var, Pol Orb, and Non Ad are abbreviations for the close-coupling approximation, variational-bound, modified variational-bound, variational, polarized-orbital, and nonadiabatic methods, respectively. A number in parentheses gives the uncertainty in the last digit.

States	Method	Singlet		Triplet
		$ka_0=0.4$	$ka_0=0.6$	$ka_0=0.4$
1s		1.2395[a]	0.8691[a]	2.2573[a]
		1.239[b]		2.257[b]
1s+2p	VB	1.2993		
	CCA[c]	1.2993		
All s	VB	1.2695	0.9100	2.2578
	Var[d]	1.2696	0.9107	2.2579
All (s+p)	VB	1.4029	1.0278	2.2922
	Var[d]	1.4001	1.0275	2.2923
Final	VB	1.4135	1.0374	2.2938
	Mod VB[e]	1.409	1.034	2.2936
	Var[d]	1.4146(6)	1.041(1)	2.2938(4)
	Pol Orb[f]	1.469		2.320
	Non Ad	1.45(6)[g]		2.2936[h]

[a] Obtained in the present calculation.
[b] See Ref. 1(a), p. 472.
[c] See Ref. 14.
[d] See Ref. 7.
[e] See Ref. 15.
[f] See Ref. 16.
[g] See Ref. 17.
[h] See Ref. 18.

the 2p state only, which corresponds to the close-coupling approximation (CCA). The VB result must be less than or equal to the CCA result. The VB calculation can easily be performed by taking only states with $l_1=1$ and setting $b_{1i}=0.5$ and using several values for d_{1i} in the trial function (2.30). The result for the 1s+2p singlet phase shift for $ka_0=0.4$ is given in Table I, and agrees with the result obtained by Fraser and McEachran,[14] who performed a CCA calculation.

In Table I we compare the results obtained for the singlet and triplet phase shifts using the VB method with those obtained using other techniques.[7,15–18] (Modifications of the VB approach which avoid the necessity of evaluating G^P have been introduced, particularly by Gailitis.[19] The advantages and disadvantages of the use of G^P are discussed in Ref. 13.) The most accurate values of the phase shifts are considered to be those obtained by Schwartz,[7] who used a modified Kohn variational scheme. The results given by Schwartz include all s alone, all (s+p), and the final phase shifts, and in all of these cases our results are somewhat lower than, but quite close to his results. The fact that our values are below those of Schwartz is not a shortcoming inherent in the VB method but rather the result of our choice of the trial function. Schwartz includes the r_{12} coordinate, which accounts more directly for the effect of the correlation of position of the two electrons. We were interested in the VB formulation for arbitrary L, and it is much simpler to do this with our choice of coordinates.

We have found no anomalies or infinities occurring in $\tan\eta$, contrary to the usual variational principles, where, as one increases the number of terms in the trial function, the "stationary" value of the phase shift does not converge smoothly, and may on occasion turn out to be grossly inaccurate. However, by proper interpretation of the calculation, the correct results can be extracted.[20] With the VB method the continuous spectrum below E has been eliminated, so that the phase shift converges monotonically to the true value. Thus the form of the trial function as well as the choice of the variational parameters which appear in it may be chosen according to a well-defined procedure.

The VB results are considerably better for e^-H scattering than for e^+H scattering. As is apparent from (2.40), a VB calculation gives a bound on Δ, and the bound on η, which is what we are really interested in, is obtained by solving (2.40) for η. The accuracy with which Δ is obtained is not necessarily reflected in the accuracy with which η is obtained. The fractional error in η is related to the fractional error in Δ by

$$\frac{\delta\eta}{\eta}\approx\frac{\delta\Delta}{\Delta}\left(\frac{\eta-\eta^P}{\eta}\right).$$

From this equation it is clear that the most favorable situation is when $\eta-\eta^P$ is small with respect to η, in which case the fractional error in η is much smaller than the fractional error in Δ. This condition holds for e^-H scattering, where the static phase shift is positive and accounts for about 90% of the final value of the phase shift, unlike the e^+H case, where the static phase shift is negative and the true phase shift is positive. Furthermore, whereas in the e^+H case the convergence in l_1 is very slow, since one has to account for the formation of virtual positronium and this is very hard to accomplish with the form of the trial function that was used, in the e^-H case the convergence in l_1 is rather fast. This explains why the CCA, while relatively ineffective in the e^+H case, is quite effective in the e^-H case. The contribution to η from the state $l_1=1$, as seen from Table II, is by far the most important one, as expected, since the induced dipole potential which varies as $1/r^4$ is the leading term in the effective long-range interaction.

In summary, the VB method gives results which are in good agreement with results obtained by other methods, with the advantage of giving rigorous lower bounds. It should be noted that recent methods have been developed for calculating upper bounds on the

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[14] R. P. McEachran and P. A. Fraser (private communication).

[15] M. Gailitis, in *Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, 1965* (Science Bookcrafters, Inc., Hastings-on-Hudson, New York, 1965), p. 10.

[16] A. Temkin and J. C. Lamkin, Phys. Rev. **121**, 788 (1961).

[17] A. Temkin, Phys. Rev. **126**, 130 (1962). (In the work by Temkin and his colleagues, the wave function is assumed to contain a restricted set of values of the angular momentum l, and the subsequent problem is solved exactly by numerical means.)

[18] A. Temkin and E. Sullivan, Phys. Rev. **129**, 1250 (1963).

[19] M. Gailitis, Zh. Eksperim. i Teor. Fiz. **47**, 160 (1964) [English transl.: Soviet Phys.—JETP **20**, 107 (1965)].

[20] C. Schwartz, Ann. Phys. (N. Y.) **16**, 36 (1961).

TABLE II. The $L=0$ phase shifts in radians for $ka_0=0.4$ obtained with the variational-bound formulation. The estimate $\tilde{\eta}$(VB) neglects the Green's function term. The η(VB) are the rigorous lower bounds on the true phase shifts obtained by restricting the virtually excited hydrogenic states to specific values of the orbital angular momentum l. The quantity n is the number of linear parameters used.

	Singlet			Triplet		
States	n	$\tilde{\eta}$(VB)	η(VB)	n	$\tilde{\eta}$(VB)	η(VB)
$1s+2p$	8		1.2993			
All s	13	1.2677	1.2695	5	2.25784	2.25784
All p	15	1.3910	1.3795	16	2.29195	2.29203
All d	13	1.2619	1.2615	7	2.25970	2.25970
All f	10	1.2455	1.2455	5	2.25767	2.25767
All g	7	1.2417	1.2417	5	2.25738	2.25738
All $(s+p)$	28	1.4120	1.4029	21	2.29214	2.29222
All $(s+p+d)$	41	1.4210	1.4112	28	2.29348	2.29356
All $(s+p+d+f)$	51	1.4229	1.4129	31	2.29365	2.29373
All $(s+p+d+f+g)$	58	1.4235	1.4135	38	2.29368	2.29376

phase shifts,[9,21,22] thus bounding the phase shifts from both sides, but these have not yet been applied.

ACKNOWLEDGMENTS

We would like to thank Dr. R. P. McEachran and Dr. P. A. Fraser for providing us with the close-coupling approximation results which were very useful in checking our computer program.

APPENDIX A: DETAILS OF THE CALCULATION

1. Form of the Matrix Elements

Since

$$PHQ=P(e^2/r_{12})Q\,, \tag{A1}$$

Eq. (2.33) can be written as

$$N_q=(2ma_0/\hbar^2)(P\Psi^P,[e^2/r_{12}]Q\Psi_{tq})\,, \tag{A2}$$

and $K_{qq'}$, defined by (2.34) can be written as

$$K_{qq'}=K_{a,qq'}+K_{b,qq'}+K_{c,qq'}\,, \tag{A3}$$

where

$$K_{a,qq'}=(2ma_0/\hbar^2)(Q\Psi_{tq},[-(\hbar^2/2m)(\nabla_1{}^2+\nabla_2{}^2) \\ -e^2(1/r_1+1/r_2)-E]Q\Psi_{tq'})\,, \tag{A4}$$

$$K_{b,qq'}=(2ma_0/\hbar^2)(Q\Psi_{tq},[e^2/r_{12}]Q\Psi_{tq'})\,, \tag{A5}$$

and

$$K_{c,qq'}=(2ma_0/\hbar^2)(Q\Psi_{tq},[(e^2/r_{12})G^P \\ \times(e^2/r_{12})]Q\Psi_{tq'})\,. \tag{A6}$$

The $1/r_{12}$ term is expanded in terms of Legendre polynomials as

$$1/r_{12}=\sum_{\lambda=0}^{\infty} S_\lambda P_\lambda(\hat{r}_1\cdot\hat{r}_2)\,, \tag{A7}$$

where

$$S_\lambda=r_<{}^\lambda/r_>{}^{\lambda+1}\,. \tag{A8}$$

The angular integrals occurring in (A2) through (A6) involve f_λ and g_λ, defined by

$$f_\lambda=f_\lambda(l_1,l_2,l_1',l_2';L)=(\mathcal{Y}_{Ll_1l_2}(\Omega_{12}),P_\lambda\mathcal{Y}_{Ll_1'l_2'}(\Omega_{12}))\,, \tag{A9}$$

and

$$g_\lambda=g_\lambda(l_1,l_2,l_1',l_2';L) \\ =(\mathcal{Y}_{Ll_1l_2}(\Omega_{12}),P_\lambda\mathcal{Y}_{Ll_1'l_2'}(\Omega_{21}))\,. \tag{A10}$$

Since

$$\mathcal{Y}_{Ll_1l_2}(\Omega_{21})=(-1)^{l_1+l_2-L}\mathcal{Y}_{Ll_2l_1}(\Omega_{12})\,, \tag{A11}$$

the relationship

$$g_\lambda(l_1,l_2,l_1',l_2';L)=(-1)^{l_1'+l_2'-L}f_\lambda(l_1,l_2,l_2',l_1';L) \tag{A12}$$

follows. We also have the relationship

$$g_\lambda=(2\lambda+1)^{-1}h_\lambda\,, \tag{A13}$$

where the f_λ and h_λ are tabulated by Percival and Seaton[23] for all transitions for which $l_1\leq 2$ and $l_1'\leq 2$. States with $l_1>2$ were also included in our trial function $Q\Psi_t$; the f_λ were evaluated by using the expression

$$f_\lambda(l_a,l_b,l_c,l_d;L)=(-1)^{l_a+l_c-L} \\ \times[(2l_a+1)(2l_b+1)(2l_c+1)(2l_d+1)]^{1/2} \\ \times\begin{pmatrix} l_a & l_c & \lambda \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_b & l_d & \lambda \\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix} l_a & l_b & L \\ l_d & l_c & \lambda\end{Bmatrix}\,. \tag{A14}$$

A tabulation of these symbols is given by Rotenberg *et al.*[24] The f's are real and satisfy the relations

$$f_0(l_1,l_2,l_1',l_2';L)=\delta_{l_1l_1'}\delta_{l_2l_2'}\,, \tag{A15a}$$

$$f_\lambda(l_1,l_2,l_1',l_2';L)=f_\lambda(l_1',l_2',l_1,l_2;L)\,, \tag{A15b}$$

and

$$f_\lambda(l_1,l_2,0,L;L)=0\,,\quad \text{if}\quad l_1\neq\lambda. \tag{A15c}$$

We introduce the operator J which interchanges l_1 and l_2, and b_q and d_q, so that for an arbitrary function $F(l_1,l_2;b_q,d_q)$,

$$JF(l_1,l_2;b_q,d_q)=F(l_2,l_1;d_q,b_q)\,, \tag{A16}$$

and we let $x_i=r_i/a_0$. Using Eqs. (2.15), (2.30), (A7), (A8), and (A15), N_q can be written as

$$N_q=(2/a_0)^{1/2}(1+\epsilon J)f_{l_1}(l_1,l_2,0,L;L) \\ \times\int dr_2w(l_2,d_q;x_2)u^P(r_2)\int dr_1r_1R(r_1)S_{l_1}w(l_1,b_q;x_1)\,. \tag{A17}$$

Using (2.30), (A7), (A8), and (A15), and introducing

$$\Lambda_i\equiv-\frac{\hbar^2}{2m}\left[\frac{d^2}{dx_i{}^2}-\frac{l_i(l_i+1)}{x_i{}^2}\right]-\frac{e^2}{x_i},\quad i=1\ \text{or}\ 2, \tag{A18}$$

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[21] L. Spruch, in *Few Nucleon Problems, Ninth Summer Meeting of Nuclear Physicists, Hercegnovi*, edited by M. Cerineo (Federal Nuclear Energy Commission of Yugoslavia, 1964).

[22] Y. Hahn, Phys. Rev. **139**, B212 (1965).

[23] I. C. Percival and M. J. Seaton, Proc. Camb. Phil. Soc. **53**, 655 (1957).

[24] M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., *The 3-j and 6-j Symbols* (The Technology Press, Massachusetts Insititute of Technology, Cambridge, Massachusetts, 1959).

we have

$$K_{a,qq'}=\frac{4m}{\hbar^2}(1+\epsilon J)\delta_{l_1l_1'}\delta_{l_2l_2'}$$

$$\times\left[\int dr_1 w(l_1,b_q;x_1)w(l_1',b_{q'};x_1)\right.$$

$$\times\int dr_2 w(l_2,d_q;x_2)(\Lambda_2-E)w(l_2',d_{q'};x_2)$$

$$+\int dr_2 w(l_2,d_q;x_2)w(l_2',d_{q'};x_2)$$

$$\left.\times\int dr_1 w(l_1,b_q;x_1)\Lambda_1 w(l_1',b_{q'};x_1)\right], \qquad \text{(A19)}$$

and

$$K_{b,qq'}=2a_0^{-1}(1+\epsilon J)\sum_{\lambda} f_\lambda(l_1,l_2,l_1'l_2';L)$$

$$\times\int dr_2 w(l_2,d_q;x_2)w(l_2',d_{q'};x_2)$$

$$\times\int dr_1 w(l_1,b_q;x_1)S_\lambda w(l_1',b_{q'};x_1). \qquad \text{(A20)}$$

Using in addition (2.24), $K_{c,qq'}$ may be written as

$$K_{c,qq'}=(2e^2/a_0)(1+\epsilon J)(1+\epsilon J')f_{l_1}(l_1,l_2,0,L;L)$$

$$\times f_{l_1'}(l_1',l_2',0,L;L)$$

$$\times\int dr_2 r_2 w(l_2,d_q;x_2)\int dr_2' r_2' g(\epsilon;r_2,r_2')w(l_2',d_{q'};x_2')$$

$$\times\int dr_1 r_1 R(r_1)w(l_1,b_q;x_1)S_{l_1}$$

$$\times\int dr_1' r_1' R(r_1')w(l_1',b_{q'};x_1')S_{l_1'}, \qquad \text{(A21)}$$

where J' exchanges l_1' and l_2', and $b_{q'}$ and $d_{q'}$, and $g(\epsilon;r,r')$ is given by (2.25).

The expression for N_q given by (A17) requires the knowledge of $u^P(r)$, the solution of the static equation (2.17). This equation was solved numerically by iteration. While the singlet case gives little trouble, the triplet case requires special treatment because of the existence of the solution $rR(r)$ of (2.17). A procedure given by Saraph and Seaton,[25] which generates a solution which is orthogonal to $rR(r)$, was used.

2. Choice of the Nonlinear Parameters

The trial function (2.30) contains two nonlinear parameters, b and d, for each linear parameter c. Certain values of b and d are not allowable since they lead to singular matrices. In the triplet case, b can not equal d, and in both the singlet and the triplet cases one cannot take two terms in the trial function with the values of b and d interchanged. Furthermore, neither b nor d can assume the value unity for $l=0$.

Two important simplifications are possible in the course of searching. The nonlinear parameters are not very sensitive to the coupling between different l states, and the search was therefore carried out for each state separately. The linear parameters are determined in the final calculation in which all coupling is taken into account. The $K_{c,qq'}$ terms, which involve the static Green's function, are neglected during the course of the searching. These terms have to be evaluated numerically and this requires over 80% of the total machine time, although their contribution to the phase shift is only a few percent.

Different methods were used to obtain the b's and d's for $ka_0=0.4$ and $ka_0=0.6$. For $ka_0=0.4$, a systematic searching procedure was used. We first searched for a one-term trial function by letting b and d run through a wide range of values and choosing that set which gave the largest value for the phase shift. Then, keeping the first term fixed, we searched for a second term. As additional terms were introduced, the old parameters were kept fixed while the new parameters were varied. This procedure was continued until the addition of more terms contributed very little to the phase shift. For $ka_0=0.6$, a procedure was used which saved much machine time, was less tedious than the previous method, and gave results which were almost as good. In this case we simply formed many sets of b's and d's for each l and chose the set that gave the largest value for the phase shift and then searched for one or two additional pairs of b's and d's as in the systematic search procedure.

It was found that as the number of terms in $Q\Psi_t$ became large, the accuracy in solving for N, defined by (2.33), was often sharply reduced owing to cancellation between elements of the matrix K, defined by (2.34), during inversion. To insure the accuracy of our calculation various checks were used, and only trial functions which gave reliable results were retained. The normalized determinant of **K**, N.D.(**K**), defined by

$$\text{N.D.}(\mathbf{K})=\frac{\det\mathbf{K}}{\prod_i K_{ii}},$$

was used as a criterion for ill-conditioning of the matrix **K**. If the addition of another term in the trial function caused a marked decrease (several orders of magnitude) in the value of N.D.(**K**), that term was rejected.

Another accuracy check was that the quantity

$$\beta\equiv\left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{\sum_j K_{ij}c_j+N_i}{N_i}\right)^2\right]^{1/2},$$

where the c's are the computed values of the linear parameters obtained from (2.51), be less than about

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[25] H. E. Saraph and M. J. Seaton, Proc. Phys. Soc. (London) **80**, 1057 (1962).

10^{-5}. A further check used was to calculate Δ from (2.36) and compare this result to the value for Δ obtained from (2.39). The inequality (2.35) holds for any c no matter how inaccurate the inversion may be, and therefore we have a rigorous result independent of the inversion error. In practice we required that the two values of Δ obtained from (2.35) and (2.39) agree to five significant figures.

APPENDIX B: MATRIX ELEMENTS FOR $L=0$

We present here expressions for the vector elements N_p and the matrix elements $K_{pq}(=K_{a,pq}+K_{b,pq}+K_{c,pq})$ defined by (2.33) and (2.34), respectively, where we replaced q by p and q' by q. The matrix elements are given for $l=0$ and $l=1$ where $l=\gamma=l_1=l_2$ for $L=0$. In the following we set $2m/\hbar^2=1$, and we use the notation

$$B_{pq}=b_p+b_q\,,\quad D_{pq}=d_p+d_q\,,$$
$$A_p=1+b_p\,,\quad T_p=1+d_p\,,$$
$$a_p=8A_p^{-3}\,,\quad t_p=8T_p^{-3}.$$

N_p and $K_{c,pq}$, defined by (A21), are given in terms of integrals involving $u^P(x)$ and $g(\epsilon;x,x')$ defined by (2.16b) and (2.25), respectively. Since $u^P(x)$ and $g(\epsilon;x,x')$ can only be obtained numerically, these integrals must be evaluated numerically. We have

$$N_p=4\sqrt{2}\int_0^\infty dx\,u^P(x)n_p(x)\,,$$

and

$$K_{c,pq}=32\int_0^\infty dxdx'n_p(x)n_q(x')g(\epsilon;x,x')\,,$$

where

$$n_p(x)=(1+\epsilon J)(-1)^l(2l+1)^{-1/2}w(l,d_p;x)$$
$$\times[Z(l,l+2,A_p;x)-a_pZ(l,2,2;x)\delta_{0l}].$$

Z is defined by

$$Z(m,n,b;x)=\int_0^\infty dx'(x_</x_>)^m(x'^n/x_>)\exp(-bx')\,,$$

which can be evaluated explicitly.[6] We may write

$$(1+\epsilon J)M_{pq}=K_{a,pq}+K_{b,pq}\,,$$

and the M's are given here in terms of the quantity I, where

$$I(m,n,b,p,d)=\int_0^\infty dx\,Z(m,n,b;x)x^pe^{-dx}.$$

This integral can also be evaluated explicitly.[6] The values of p and q in the matrix elements correspond to the first and second pairs of subscripts on the M's, respectively.

$$\begin{aligned}M_{i0i'0}={}&8(B_{pq}D_{pq})^{-3}[b_pb_q+d_pd_q-B_{pq}-D_{pq}-(k^2-1)]-a_pa_qD_{pq}^{-3}(d_pd_q-D_{pq}-k^2)-t_pt_qB_{pq}^{-3}(b_pb_q-B_{pq}-k^2)\\&-\tfrac{1}{8}a_pa_qt_pt_q(1+k^2)+4[I(0,2,B_{pq},2,D_{pq})-a_pI(0,2,A_q,2,D_{pq})-a_qI(0,2,A_p,2,D_{pq})-t_pI(0,2,B_{pq},2,T_q)\\&-t_qI(0,2,B_{pq},2,T_p)+a_pa_qI(0,2,2,2,D_{pq})+a_pt_qI(0,2,A_p,2,T_p)+a_pt_pI(0,2,A_q,2,T_q)+t_pt_qI(0,2,B_{pq},2,2)\\&+a_qt_pI(0,2,A_p,2,T_q)+a_qt_qI(0,2,A_p,2,T_p)-a_pa_qt_qI(0,2,2,2,T_p)-a_qt_pt_qI(0,2,2,2,A_p)\\&\qquad-a_pa_qt_pI(0,2,2,2,T_q)-a_pt_pt_qI(0,2,2,2,A_q)+a_pa_qt_pt_qI(0,2,2,2,2)]\,,\end{aligned}$$

$$M_{i1i'0}=-4\times3^{-1/2}[I(1,3,B_{pq},3,D_{pq})-a_qI(1,3,A_p3,D_{pq})-t_qI(1,3,B_{pq},3,T_p)+a_qt_qI(1,3,A_p,3,T_p)]\,,$$

$$M_{i1i'1}=2(4!)^2(B_{pq}D_{pq})^{-5}[b_pb_q+d_pd_q-\tfrac{1}{2}(B_{pq}+D_{pq})-(k^2-1)]+[I(0,4,B_{pq},4,D_{pq})+(2/5)I(2,4,B_{pq},4,D_{pq})].$$