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Configuration-Space Hamiltonian for Heavy Atoms and Correction to the Breit Interaction*

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The lowest-order configuration-space Hamiltonian (CSH) for a heavy atom is constructed from quantum electrodynamics by a variational procedure. A variational potential function Ω is introduced which in effect allows some freedom in the choice of the definition of the difference between electrons and positrons. The optimization of Ω results in a nonlinear equation from which it is shown that Ω is probably not small for relativistic electrons. The procedure results in a CSH which contains a new two-body interaction which is relativistic in origin and which is apparently of the same order of magnitude as the Breit interaction when acting between relativistic electrons.

I. INTRODUCTION

In the first paper of this series (I)[1] the problem of the extraction of a configuration-space Hamiltonian (CSH) for a heavy atom from the usual quantum-electrodynamic (QED) formulation of the problem was discussed. A review of the existing situation was presented. The fact that the most obvious generalization of the Schrödinger CSH, a sum of single-particle Dirac Hamiltonians with simple two-body interactions, leads to difficulties[2] (Brown's disease) was reviewed. The three-electron potential interactions were derived for the situation where there are only a few electrons (i.e., where $N\alpha \ll 1$, here N is the number of electrons). The assumption was then made that the derived form applies even when there are many electrons and that the total energy residing in the three-body potential would then be the sum of this form over all different triplets of electrons in the atom. In that case it was possible to show that the total three-body energy is of the order of a few rydbergs, a small part of the total energy of the atom.

We now return to the problem of the CSH of a heavy atom retaining only lowest-order terms. For example, we shall find the leading two-body potential will be of order e^2 but there will be corrections to the two-body interaction of order e^4 and smaller. These will be neglected. For this reason we shall never encounter renormalization problems here. However, extension of this work will run into these problems and it is not obvious how they will best be handled. We shall also neglect three-body potentials because of the author's previous work.[1] This is not completely justified since the three-body results described in I depend on the form of the two-body potential and this form changes in the many electron system considered here from the form for the few electron system in I. Thus our neglect of the three-body potentials here is not rigorous and will have to be reinvestigated subsequently.

A method for obtaining a CSH would be to expand the Fock-space wave function in an infinite series of terms. The first has N electrons, the second $N+1$ electrons and one positron, and each additional term has an extra pair. The amplitude function of the first term may then be considered the wave function of the atom. We can then obtain an infinite set of equations coupling all the amplitude functions. We could eliminate all but the first, thereby obtaining the required Hamiltonian but this procedure would result in an intractable operator (if it exists at all). We take the point of view here that the elimination of even one other function would complicate the resulting CHS beyond the point of usefulness. Therefore we seek an expression for the Fock-space wave function which contains only

a single (N-electron) amplitude function. As was pointed out in I, there is still a great deal of freedom contained in such a function. This freedom may be described as the ambiguity in the definition of the distinction between an electron and positron. The usual definition is accomplished by choosing a complete set of states and arbitrarily dividing them into two categories labeling one electron and the other positron. The usual choice of complete set is the eigenstates of the free-particle Dirac Hamiltonian, and the usual division line is at zero energy. This last is useful since this separates the electrons from positrons by a large gap in the spectrum ($2mc^2$) (and makes the total energy positive in a simple way) thereby mirroring the physical statement that electrons and positrons are different entities. We shall maintain this division line but we will insert a single-particle potential Ω into the Dirac Hamiltonian which defines the complete set for the single-particle representation of the operators. We shall then attempt to find an optimum form for Ω within the assumed form of the Fock-space wave function.

It is clear that the results of the exact theory are independent of Ω but since we will be severely constrained by the form of the wave function outlined above, our results will depend upon Ω. Indeed we shall see that the result is an addition to the two-body interaction which is not of the Breit form,[3] and is apparently not small compared with it. We interpret it as a modification of the usual electron-electron interaction by the medium in which they are imbedded, the rest of the electrons.

In Sec. II we derive the CSH. In Sec. III we find the optimum Ω and find that its contribution to the two-body potentials in the CSH are apparently of the same order of magnitude as the usual Breit interaction. A brief discussion of the results is contained in Sec. IV.

II. DERIVATION OF CSH

Our starting point[1] is the Schrödinger equation of QED for the electron-positron field and the radiation field in the presence of an infinitely heavy point nucleus with charge number Z,

$$(E - H)\Psi = 0 , \tag{2.1}$$

where H is written in the Coulomb gauge and in a somewhat unusual form

$$H = H_0 + H_c' + H_I . \tag{2.2}$$

The zero-order Hamiltonian which defines the representation in which we work is

$$H_0 = \int d^3x \bar{\psi}(x) , \gamma_4(h_0(x)\delta(x - x') + \Omega(x, x')) \times \psi(x') d^3x' + H_{\text{rad}} , \tag{2.3}$$

where the usual Dirac Hamiltonian is

$$h_0(x) = C\vec{\alpha} \cdot \vec{p} + \beta mC^2 - ze^2/x \tag{2.4}$$

and H_{rad} describes the noninteracting photon field. The modified Coulomb interaction is

$$H_C' = H_C - H_\Omega , \tag{2.5}$$

where H_Ω is the counter term just canceling the Ω term in H_0 and the usual Coulomb interaction is

$$H_C = \tfrac{1}{2} \int d^3x \bar{\psi}(x)\gamma_4\psi(x) \frac{e^2}{|x - x'|} \bar{\psi}(x')\gamma_4\psi(x')d^3x' . \tag{2.6}$$

Finally, the transverse matter-photon interaction is

$$H_I = - \int d^3x \vec{j}(x) \cdot \vec{A}(x). \tag{2.7}$$

We now construct a trial wave function in Fock space of the form

$$\Psi = e^{-i\sigma}\Psi' , \quad \Psi' = \int (d^3x)^N \Phi(x_1 \cdots x_N)\Lambda_+(x_1, x_1') \cdots \Lambda_+(x_N, x_N')\psi^\dagger(x_1') \cdots \psi^\dagger(x_N')(d^3x')^N |0\rangle, \tag{2.8}$$

where $|0\rangle$ is the matter-photon vacuum state[4] and Λ_+ is a positive-frequency projection operator[5] defined by

$$\Lambda_+(1, 1') = \sum_n^+ \phi_n(1)\phi_n^*(1') , \tag{2.9}$$

where the ϕ_n are eigenstates of the zero-order Hamiltonian

$$(h_0 + \Omega - \mathcal{E}_n)\phi_n = 0 , \tag{2.10}$$

and where the sum in (2.9) is restricted to eigenstates of (2.10) for which $\mathcal{E}_n > 0$. This restriction is just the implementation of the dividing line mentioned in the preceding section. The factor $e^{-i\sigma}$ is the result of the contact transformation in the interaction representation which decouples the matter and radiation fields to lowest order. It is given by

$$\sigma = \tfrac{1}{2} \int_{-\infty}^{\infty} d\tau \, \epsilon(\tau) \, e^{-iH_0\tau} H_I e^{iH_0\tau} , \tag{2.11}$$

where $\epsilon(\tau) = \text{sgn}(\tau)$. Note that the factor $e^{-i\sigma}$ generates terms in Ψ [Eq. (2.8)] with an arbitrary number of pairs but in a very special way. There are other ways of accomplishing this decoupling but this seems to be the simplest.

This wave function is now inserted into a Rayleigh-Ritz variational expression which is equivalent to Eq. (2.1):

$$E = \frac{\langle \Psi, H\Psi \rangle}{\langle \Psi, \Psi \rangle} = \frac{\langle \Psi', H'\Psi' \rangle}{\langle \Psi', \Psi' \rangle} , \tag{2.12}$$

where

$$H' = e^{i\sigma}He^{-i\sigma}$$
$$= H_0 + e^{i\sigma}(H_C - H_\Omega)e^{-i\sigma} + \sum_{n=1}^{\infty} i^n \frac{n}{(n+1)!} C_n[\sigma, H_I], \tag{2.13}$$

where C_n is the repeated commutator of H_I with σ, n times. The wave function Φ and the potential Ω will now be optimized by use of the stationary principle $\delta E = 0$.

We note that the photon-vacuum expectation value is taken in (2.12), that we are dropping higher-order terms in the sense described in Sec. I and that three-body and higher interactions will be neglected. With these restrictions the term $e^{i\sigma}H_Ce^{-i\sigma}$ can be replaced by H_C. For the H_Ω term we expand in powers of σ yielding

$$e^{i\sigma}H_\Omega e^{-i\sigma} = \sum_{n=0}^{\infty} \frac{i^n}{n!} C_n[\sigma, H_\Omega].$$

The first term ($n=0$) in the sum just cancels the H_Ω term in H_0, the $n=1$ term is off diagonal in photon operators and is dropped and the $n=2$ term yields a contribution to H' of the form

$$\tfrac{1}{2}[\sigma, [\sigma, H_\Omega]] \to \tfrac{1}{2}\sum N(b_n^+ b_l^+ b_{l'} b_{n'}) C_{nl,n'l'}, \tag{2.14}$$

where N is the normal ordering operator and the Hermitian operator C is given by

$$C_{nl,n'l'} = 2\sum_m \left(\frac{\eta_{ln,mn'} - \eta_{nl,n'm}}{\mathcal{E}_{n'n} + \mathcal{E}_{ml}} \Omega_{ml'} - \Omega_{l'm} \frac{\eta_{mn,l'n'} - \eta_{ln,n'l'}}{\mathcal{E}_{n'n} + \mathcal{E}_{l'm}} \right). \tag{2.15}$$

Here $\mathcal{E}_{n'n} = \mathcal{E}_{n'} - \mathcal{E}_n$ and

$$\Omega_{ml} = \int d^3x \bar{\phi}_m(x)\gamma_4 \Omega(x, x')\phi_l(x')d^3x' \tag{2.16}$$

and η is the elementary two-body transverse interaction given (I) by

$$\eta_{nl,n'l'} = \tfrac{1}{4}e^2 \int d^3x_1 d^3x_2 \bar{\phi}_n(x_1)\gamma_{\mu_1}\phi_{n'}(x_1)\bar{\phi}_l(x_2)\gamma_{\mu_2} \times \phi_{l'}(x_2)[\delta_{\mu_1\mu_2}\nabla^2 - \nabla_{\mu_1}\nabla_{\mu_2}] x_{12}\left(\frac{2\hbar c}{x_{12}\mathcal{E}_{n'n}} \sin\frac{x_{12}\mathcal{E}_{n'n}}{2\hbar c}\right)^2. \tag{2.17}$$

The b's are the creation and destruction operators obtained from

$$b_n = \int d^3x \, \phi_n^*(x)\psi(x). \tag{2.18}$$

The $n=1$ term of the sum in (2.13) is just the usual transverse two-body interaction which can be combined with H_c and written as

$$\tfrac{1}{2}\sum N(b_n^+ b^+_l b_{l'} b_{n'}) A_{nl,n'l'}, \tag{2.19}$$

where

$$A_{nl,n'l'} = \langle nl|(e^2/x_{12})|n'l'\rangle - \eta_{nl,n'l'} - \eta_{ln,l'n'}. \tag{2.20}$$

We note that the new term generated by Ω [Eq. (2.14)] is a two-body term which just addeds to Eq. (2.20) and that if Ω is of order e^2 or smaller then C is negligible according to the rules established in Sec. I.

However if Ω is not small then C presents a modification of the Breit interaction between two electrons in an atom. The matrix elements in (2.12) may now be simplified with the result

$$E = \langle \Phi_+, [\sum_{j=1}^{N} \Lambda_+(j)h_0(j)\Lambda_+(j) + \sum_{i>j=1}^{N} \Lambda_+(i)\Lambda_+(j)\upsilon(ij)\Lambda_+(i)\Lambda_+(j)]\Phi_+\rangle / \langle \Phi_+, \Phi_+\rangle, \tag{2.21}$$

where

$$\Phi_+ = \Lambda_+(1)\cdots\Lambda_+(N)\Phi,$$

h_0 is given by (2.4) and υ is the total two-body interaction given by

$$\upsilon(12, 1'2') = \sum \phi_n(1)\phi_l(2)[\langle nl|(e^2/x_{12})|n'l'\rangle - \eta_{nl,n'l'} - \eta_{ln,l'n'} + \tfrac{1}{2}C_{nl,n'l'} + \tfrac{1}{2}C_{ln,l'n'}]\phi_{n'}^*(1')\phi_{l'}^*(2'). \tag{2.22}$$

Variation[4] of (2.21) with respect to Φ yields the CSH and the Schrödinger equation

$$(E - H_{CS})\Phi_+ = 0 \tag{2.23}$$

with

$$H_{CS} = \sum_{i=1}^{N} \Lambda_+(i)h_0(i)\Lambda_+(i) + \sum_{i>j=1}^{N} \Lambda_+(i)\Lambda_+(j)\upsilon(i,j)\Lambda_+(i)\Lambda_+(j). \tag{2.24}$$

This is the CSH we set out to find. It is essentially a sum of single-particle Dirac Hamiltonians (with the nuclear Coulomb potential included) plus a two-body interaction surrounded by positive-frequency projection operators to prevent "Brown's disease."[1] The effect of the positive-frequency projection operators around h_0 are small, since $\Lambda_+ = 1 - \Lambda_-$ and the Λ_- operator is important only for relativistic single-particle states. The two-body potential depends upon Ω through the states in (2.22), or through the h operator in (3.10). In addition there is the linear dependence of C on Ω which we shall see provides a new potential, added to the Breit interaction (η) which is probably not negligible compared with it.

III. OPTIMIZATION OF Ω

Variation with respect to Ω will yield an equation for the determination of Ω. For that purpose we rewrite (2.21) by using the antisymmetry of Φ_+:

$$E=\frac{N\langle\Phi_+,\,(\Lambda_+(1)h_0(1)\Lambda_+(1)+\tfrac{1}{2}(N-1)\Lambda_+(1)\Lambda_+(2)\upsilon(12)\Lambda_+(1)\Lambda_+(2))\Phi_+\rangle}{\langle\Phi_+,\,\Phi_+\rangle}\,. \tag{3.1}$$

We define one- and two-particle density matrices by

$$\rho_1(1,1')=\int d^3x_2\cdots d^3x_N\,\Phi_+^*(1,2\ldots,N)\Phi_+(1'2\ldots,N)\,,$$

$$\rho_2(12,1'2')=\int d^3x_3\cdots d^3x_N\,\Phi_+^*(1,2,3\ldots,N)\Phi_+(1',2',3\ldots,N)\,, \tag{3.2}$$

yielding[4]

$$E=\frac{N\mathrm{tr}[\Lambda_+h_0\Lambda_+\rho_1+\tfrac{1}{2}(N-1)\Lambda_+(1)\Lambda_+(2)\upsilon(12)\Lambda_+(1)\Lambda_+(2)\rho_2]}{\langle\Phi_+,\,\Phi_+\rangle}\,, \tag{3.3}$$

where tr indicates the trace over all free coordinates. We now vary (3.3) with respect to Ω. Using (2.9) and (2.10), we obtain

$$\delta\Lambda_+=\Lambda_-Q\Lambda_++\Lambda_+Q^+\Lambda_-\,, \tag{3.4}$$

where

$$Q=\int_0^\infty dv\,e^{hv}\,\delta\Omega e^{-hv}\,, \tag{3.5}$$

with

$$h=h_0+\Omega\,. \tag{3.6}$$

The quantities ρ_1 and ρ_2 are not varied since $(\delta\Phi)_+$ is independent of $\delta\Omega$ in the variation process so that this variation of E comes from variation of Λ_+ and $\upsilon(12)$. If we consider the Λ_+ variation first, the substitution of (3.4) into δE results in[4]

$$\frac{N\mathrm{tr}[(Q^+\Lambda_-h+h\Lambda_-Q)\rho_1+\tfrac{1}{2}(N-1)(Q^+(1)\Lambda_-(1)+Q^+(2)\Lambda_-(2))\upsilon(12)\rho_2+\tfrac{1}{2}(N-1)\upsilon(12)(\Lambda_-(1)Q(1)+\Lambda_-(2)Q(2))\rho_2]}{\langle\Phi_+,\,\Phi_+\rangle}\,, \tag{3.7}$$

where we have used the result obtained from (2.23):

$$\Lambda_-\rho_1=\Lambda_-\rho_2=0\,. \tag{3.8}$$

Using the symmetry of ρ_2 and υ in their arguments this may be rewritten as

$$\frac{N\int_0^\infty dv\,\mathrm{tr}\delta\Omega(1)[\Lambda_-e^{hv}h_0\rho_1e^{-hv}+e^{-hv}\rho_1h_0e^{hv}\Lambda_-+(N-1)e^{h(1)v}\Lambda_-(1)\upsilon\rho_2e^{-h(1)v}+(N-1)e^{-h(1)v}\rho_2\upsilon\Lambda_-(1)e^{h(1)v}]}{\langle\Phi_+,\,\Phi_+\rangle}\,. \tag{3.9}$$

Before proceeding with the variation of υ it is useful to write it in a more compact operator form. Equation (2.22), after some straightforward manipulation becomes

$$\upsilon(12)=\frac{e^2}{x_{12}}+\tfrac{1}{4}e^2\int_{-\infty}^{\infty}dt[e^{-ih(1)t}f(12,t)e^{ih(1)t}+e^{-ih(2)t}f(12,t)e^{ih(2)t}]+ie^2\int d(tu)[e^{iq(12)}f(12,t-u)e^{-iq(12)},\,\Omega(2)-\Omega(1)]. \tag{3.10}$$

The second term is just the operator form of the transverse interactions [the η term in (2.22)] and $f(12,t)$ is defined by

$$\int_{-\infty}^{\infty}f(12,t)e^{-i\mathcal{E}t}=-(\alpha^{(1)}\cdot\alpha^{(2)}\nabla^2-\alpha^{(1)}\cdot\nabla\alpha^{(2)}\cdot\nabla)\times x_{12}\left(\frac{\hbar c}{x_{12}\mathcal{E}}\sin\frac{x_{12}\mathcal{E}}{2\hbar c}\right)^2\,. \tag{3.11}$$

The last term in (3.10) comes from the C terms in (2.22). It represents the new electron-electron interaction. The exponential factors are given by

$$q(12)=th(1)+uh(2)\,, \tag{3.12}$$

and the domain of integration in the (t,u) plane is defined by

$$\int d(tu)=\int_0^\infty du\int_{-\infty}^0 dt-\int_0^\infty dt\int_{-\infty}^0 du\,. \tag{3.13}$$

Variation of υ with respect to Ω may now be accomplished by noting that f is independent of Ω and by the use of

$$\delta e^a=\int_0^1 d\lambda\,e^{a\lambda}\delta a e^{a(1-\lambda)}\,. \tag{3.14}$$

After some lengthy algebra we obtain the contribution to δE from the variation of υ:

$$N(N-1)\left(\frac{ie^2}{4}\int_{-\infty}^{\infty}t\,dt\int_0^1 d\lambda\,\mathrm{tr}\delta\Omega(1)e^{-ih(1)t\lambda}[e^{ih(1)t}f(12,t)e^{-ih(1)t},\,\rho_2(12)]\,e^{ih(1)t\lambda}\right.$$

$$-ie^2\int d(tu)\,\mathrm{tr}\,\delta\Omega(1)[\rho_2(12),\, e^{iq(12)}f(12,\,t-u)e^{-iq(12)}]$$

$$+ie^2\int d(tu)\int_0^1 d\lambda\,\mathrm{tr}\,\delta\Omega(1)it\{e^{i(1-\lambda)q(12)}f(12,\,t-u)e^{-iq(12)}\,[\Omega(2)-\Omega(1),\,\rho_2(12)]\,e^{i\lambda q(12)}$$

$$-e^{-i\lambda q(12)}\,[\Omega(2)-\Omega(1),\,\rho_2(12)]\,e^{iq(12)}f(12,\,t-u)e^{-i(1-\lambda)q(12)}\}\Big)\langle\Phi_+,\,\Phi_+\rangle^{-1}\ . \quad (3.15)$$

The equation $\delta E=0$ may now be written by adding the expressions (3.9) and (3.15) and setting them equal to zero. Now we note that $\delta\Omega(1)$ is an arbitrary function so its coefficient in the trace over index 1 must vanish. The resulting equation is

$$\int_0^\infty dv\, e^{h(1)v}\Lambda(1)[-\Omega(1)\rho_1(1)+(N-1)\,\mathrm{tr}_2 v(12)\rho_2(12)]\,e^{-h(1)v}$$

$$+\tfrac{1}{8}ie^2(N-1)\int_{-\infty}^{\infty}t\,dt\int_0^1 d\lambda\,e^{-ih(1)t\lambda}\,\mathrm{tr}_2[e^{ih(1)t}f(12,\,t)e^{-ih(1)t},\,\rho_2(12)]\,e^{ih(1)t\lambda}$$

$$+\tfrac{1}{2}ie^2(N-1)\int d(tu)\,\mathrm{tr}_2[e^{iq(12)}f(12,\,t-u)e^{-iq(12)},\,\rho_2(12)]$$

$$-\tfrac{1}{2}e^2(N-1)\int d(tu)\,t\int_0^1 d\lambda\,\mathrm{tr}_2\,e^{-i\lambda q(12)}\,[e^{iq(12)}f(12,\,t-u)e^{-iq(12)},[\Omega(2)-\Omega(1),\,\rho_2]]\,e^{i\lambda q(12)}+\mathrm{H.c.}=0\ , \quad (3.16)$$

where we have used the relation $\Lambda_-h_0\Lambda_+=-\Lambda_-\Omega\Lambda_+$.

Evidently the solution of this equation for Ω is a formidable task. We shall not attempt it here but instead we assume that Ω is small and expand in it. This will yield a linear integral equation for Ω which is still not readily solvable. However we can give a plausible argument to show that the solution of the equation for Ω is not small violating our initial assumption. This indicates that Ω is not small and therefore that the new terms in (2.22) representing a modified electron-electron interaction are probably not negligible.

Before proceeding we note that all terms in (3.16) are relativistic in origin. This is readily seen since f [Eq. (3.11)] is the result of a transverse photon interaction and the first term in (3.16) depends upon the connection between (−) and (+) states by the operators Ω and $v(12)$. The factor $(N-1)$ is simply illustrated by replacing ρ_1 and ρ_2 by those resulting from a Slater determinant approximation to Φ_+. In that case it becomes evident that the factor $(N-1)$ gets replaced by a sum over orbitals, and that only the relativistic orbitals contribute significantly.[1] Therefore the factor $(N-1)$ is roughly replaced by N_r, the number of relativistic electrons in the atom (as in Ref. 1). Ω is then relativistic in origin, entering H_{CS} through v [(3.10)] and Λ_+. These are also relativistic effects which are probably not of overriding importance in H_{CS} so that Φ_+ is probably a slowly varying function of Ω. For this reason ρ_1 and ρ_2 will not be expanded in Ω.

If we project with $\Lambda_+(1)$ on both sides of (3.16) the first term vanishes. We may then linearize the remaining terms (which are explicitly Hermitean) with the aid of the lemma: If $a=a_0+\Delta$, then

$$e^{ia}ge^{-ia}=e^{ia_0}ge^{-ia_0}$$

$$+i\int_0^1 d\xi\,[e^{it a_0}\Delta e^{-it a_0},\,e^{ia_0}ge^{-ia_0}]+O(\Delta^2)\ . \quad (3.17)$$

The result is

$$\tfrac{1}{4}i\int_{-\infty}^{\infty}t\,dt\int_0^1 d\lambda\,e^{-ih(1)t\lambda}\,\mathrm{tr}_2[e^{ih(1)t}f(t)e^{-ih(1)t},\,\rho_2]\,e^{ih(1)t\lambda},+i\int d(tu)\,\mathrm{tr}_2[e^{iq}f(t-u)e^{-iq},\,\rho_2]$$

$$+\tfrac{1}{4}\int_{-\infty}^{\infty}t^2\,dt\int_0^1\lambda\,d\lambda\int_0^1 d\xi\,\mathrm{tr}_2[e^{-ih(1)t\lambda\xi}\,\Omega(1)e^{ih(1)t\lambda\xi},\,e^{-it\lambda h(1)}[e^{ih(1)t}f(t)e^{-ih(1)t},\,\rho_2]\,e^{ih(1)t\lambda}]$$

$$-\tfrac{1}{4}\int_{-\infty}^{\infty}t^2\,dt\int_0^1 d\lambda\int_0^1 d\xi\,e^{-ih(1)t\xi}\,\mathrm{tr}_2[\,[e^{ih(1)t\xi}\Omega(1)e^{-ih(1)t\xi},\,e^{ih(1)t}f(t)e^{-ih(1)t}],\,\rho_2]\,e^{ih(1)t\lambda}$$

$$-\int d(tu)\int_0^1 d\lambda\,\mathrm{tr}_2[\,[e^{i\lambda q}(t\Omega(1)+u\Omega(2))\,e^{-i\lambda q},\,e^{iq}f(t-u)e^{-iq}],\,\rho_2]$$

$$-\int d(tu)t\int_0^1 d\lambda\,\mathrm{tr}_2\,e^{-i\lambda q}\,[e^{iq}f(t-u)e^{-iq},\,[\Omega(2)-\Omega(1),\,\rho_2]]\,e^{i\lambda q}=0\ , \quad (3.18)$$

where the $\langle+|\ |+\rangle$ matrix element is implied.

Here Ω has been extracted explicitly so that all other quantities are now evaluated at $\Omega=0$. Notice that the equation is homogeneous in ρ_2 and that the correlations in ρ_2 are crucial to the equation. If Φ_+ is a product of uncorrelated orthogonal orbitals

then ρ_2 is proportional to the unit matrix and the equation becomes an identity. However, even the correlations introduced by the Pauli principle in the Slater determinant form of Φ_+ are sufficient to give the equation content. In order to get an order of magnitude estimate for Ω we shall make this approximation. That is, we take Φ_+ to be a Slater determinant of orbitals and for additional simplicity take the orbitals to be eigenfunctions of h_0 (Coulomb-Dirac functions). Then the matrix elements of ρ_2 in any single-particle basis are

$$\langle \alpha\beta | \rho_2 | \alpha'\beta' \rangle = \frac{1}{N(N-1)} [\delta_{\alpha\alpha'}\delta_{\beta\beta'} - \delta_{\beta\alpha'}\delta_{\alpha\beta'}] ,$$
$$\alpha, \alpha', \beta, \beta' \leq N \qquad (3.19)$$

and since the first term is proportional to the unit matrix it does not contribute in (3.18). If we take the $\langle s | \ | s' \rangle$ matrix element of (3.18) (s and s' are both positive energy states) the result after extensive calculation is

$$\sum_b \langle sb | F(\mathcal{E}_{sb}) - F(\mathcal{E}_{bs'}) | bs' \rangle + \tfrac{1}{3} \sum_{ab} \Big(X_{sa} \langle ab | F(\mathcal{E}_{sb}) - F(\mathcal{E}_{bs'}) + \frac{\mathcal{E}_{ss'}}{\mathcal{E}_{as'}} (F(\mathcal{E}_{bs'}) - F(\mathcal{E}_{ab})) | s'b \rangle$$
$$+ X_{as'} \langle sb | F(\mathcal{E}_{bs'}) - F(\mathcal{E}_{sb}) + \frac{\mathcal{E}_{ss'}}{\mathcal{E}_{sa}} (F(\mathcal{E}_{bs}) - F(\mathcal{E}_{ab})) | ba \rangle$$
$$- X_{ab} \langle sb | F(\mathcal{E}_{sb}) - F(\mathcal{E}_{bs'}) + F(\mathcal{E}_{as'}) - F(\mathcal{E}_{sa}) | as' \rangle \Big) = 0 . \qquad (3.20)$$

Here

$$X_{ab} = \Omega_{ab} / \mathcal{E}_{ab} \qquad (3.21)$$

and $F(\mathcal{E})$ is the Fourier transform of $f(t)$ given by the right-hand side of (3.11). The sums in (3.20) extend only over the N-occupied (positive-energy) orbitals of Φ so that (3.20) is a finite set of linear algebraic equations for the unknowns X_{ab}.

The structure of the difference of two F functions was encountered in I. Each F is essentially the two-body potential due to the exchange of a transverse photon and its matrix element is proportional to $(v/c)_1(v/c)_2$ (through the α factors). It is therefore important only for relativistic states. The fact that we always encounter the difference of F's in (3.20) further reduces the contribution but we note and emphasize that this structure occurs in both the inhomogeneous term and in the kernel of (3.20). Thus the unknown X is essentially the ratio of the same kind of structures. When only one of s and s' is relativistic then the inhomogeneous term is small ($\sim v/c$) but in the sum over (a, b) in the homogeneous term there will occur matrix elements of (F-F) between states all of which are relativistic and such matrix elements are not small. Hence the X for nonrelativistic states will be small.

On the other hand, if both s and s' are relativistic then the inhomogeneous term and the kernel are the same order of magnitude and so X is of the order of unity. Then $\Omega_{ss'}$ is the order of $\mathcal{E}_{ss'}$, the difference of two relativistic energies which is a fraction of mc^2. Consequently we may expect that the single-particle potential Ω is of the order of the nuclear potential $\sim (z\alpha)^2\, mc^2$ for relativistic electrons. This conclusion is of course not valid since the result violates the assumption that Ω is small which allowed us to linearize (3.16) to obtain (3.20). However it does show that Ω is probably not small for relativistic states and that the new two-body potential in (2.22) is not negligible compared with the Breit interactions [the η's in (2.22)] for relativistic electrons.

The Breit interaction is relativistic (2.17) containing a factor $(v/c)_1 (v/c)_2$ explicitly. The new term (C) [Eq. (2.15)] contains these factors in η and in addition the potential Ω. So we may expect that these new terms are "more relativistic" than the Breit terms and die off in importance relative to the Breit term as the electrons become more nonrelativistic. The new terms are therefore probably less important than the Breit terms in the over-all structure of the atom but may be just as important for the inner electrons.

IV. DISCUSSION

The main results of this paper are summarized by the CSH, [Eq. (2.24)], and the two-body potential [Eq. (2.22)]. The optimization procedure in Sec. III is then used to define Ω which is needed to define the CSH and (12). We have raised the very strong possibility that the additional two-body interaction obtained is as important as the Breit interaction for inner electrons.

There still remain some rather unpleasant features of this formalism embodied in the nonlinearity of the results. The CSH depends weakly upon Φ through the ρ dependence of Ω. Strictly speaking this results in the statement that different states of the same atom are not orthogonal. This is unpleasant, but true. The atom is not an isolated system. It is coupled to the radiation field which is eliminated from the Hamiltonian by the approximate decoupling of the radiation and matter fields. The state of the atom will affect the state of the

radiation field. For example, if the ground state is spherically symmetric the field state will be different from an excited state with a quadrupole field. It is only the atom plus radiation field which has orthogonal states. Fortunately this is a weak effect and without the loss of significant accuracy one may chose ρ_1 and ρ_2 to be formed from, say, the ground state of the atom in which case the atomic states are orthogonal.

We have exploited the freedom of the representation of $\psi(x, t)$ and the consequent freedom of the definition of the electron in obtaining the CSH. A similar freedom exists for the radiation field. That is, (2.8) describes a photon vacuum but the photons discussed are described as plane waves. This is clearly not the optimum quantization basis for the photon field. We can exploit this freedom of definition of the photon (and the photon vacuum) in the same way as we have introduced Ω here. This will modify the two-body interaction, since it will no longer be plane wave photons which are exchanged and there may well be other effects. We shall return to this matter subsequently.

The nonlinear equation for Ω, (3.16) may not be linearized in the straightforward way that led to (3.18) since $\Omega_{ss'}$ is not small when s and s' are relativistic. However it is possible to linearize for the nonrelativistic components and for Ω_{-+} which we can show is small. We shall also return to this later.

The CSH may be reduced to its nonrelativistic form by the usual "two-component" reduction of the wave function. The new effects we have introduced here will yield new terms there which are probably small compared with previous relativistic corrections. This will have to be investigated.

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[1]M. H. Mittleman, Phys. Rev. A 4, 893 (1971). The same notation and definitions are used here.

[2]G. E. Brown and D. G. Ravenhall, Proc. Roy. Soc. (London) A208, 552 (1951).

[3]See J. B. Mann and W. R. Johnson, Phys. Rev. A 4, 41 (1971) for a recent review of the differences between the various forms of the Breit interaction.

[4]The vacuum state for the matter field is defined by the relations $\Lambda_+\Psi|0\rangle = \Lambda_-\Psi^+|0\rangle = 0$ which says that the destruction of either an electron or a positron in the vacuum annihilates the state. These definitions depend upon the definition of the electron and may be considered constraints on the vacuum, $|0\rangle$, and Ω. They are however holonomic constraints and are explicitly eliminated in arriving at (2.21) and so need not be considered further.

[5]The symbols Ω, Λ_+, etc., are used interchangeably for the operator and their configuration-space representations $\Omega(x,x')$, $\Lambda_+(x,x')$, etc. This should lead to no confusion in context.

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Upper and Lower Bounds to the Eigenvalues of Two-Electron Atoms: Proof That the $2\,^{1,3}S$ States of H^- Are Not Bound*

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We propose a new type of expansion for obtaining accurate wave functions for $^{1,3}S$ states of two-electron atoms, expressing Ψ as a sum of "configurations" of the form $(1 \pm P_{12}) \exp(-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12})$. Matrix elements of both H and H^2 can be easily evaluated for these configurations. Results of an illustrative calculation of the $2\,^{1,3}S$ states of H^-, which proves them to be unbound, are given.

We have found that trial wave functions of the form $\Psi = \sum_i C_i \psi_i$, with "configurations"

$$\psi_i = \{\exp(-\alpha_i r_1 - \beta_i r_2) \pm \exp(-\beta_i r_1 - \alpha_i r_2)\}\exp(-\gamma_i r_{12}),$$

can give very accurate eigenvalues and eigenfunctions for the ground and excited $^{1,3}S$ states of two-electron atoms. The set of parameters $\{\alpha_i, \beta_i, \gamma_i\}$ were either generated by (a) a random-number generator on (0,1) followed by a mapping onto physically realistic ranges of values, (b) direct choice of what we think should be "good" values, (c) direct optimization of a small set which minimizes the energy, or (d) a combination of these approaches. The form of the trial wave function