PHYSICAL REVIEW A

GENERAL PHYSICS

THIRD SERIES, VOLUME 24, NUMBER 3 SEPTEMBER 1981

# Theory of relativistic effects on atoms: Configuration-space Hamiltonian

Marvin H. Mittleman*

*Frederick Alexander University, Erlangen, West Germany*

(Received 21 May 1980)

The configuration-space Hamiltonian for a many-electron atom is derived clearing up some of the ambiguities concerning the projection operators which must occur in this Hamiltonian. In the process, numerical calculations which have been previously performed are justified. The elementary two-electron interaction in the presence of many other electrons is also discussed.

## I. INTRODUCTION

All numerical calculations[1] of atomic structure in the relativistic regime start from a configuration-space Hamiltonian of the form

$$H=\sum_{j=1}^{N}h(j)+\sum_{j>i=1}^{N}V(i,j)\,, \tag{1.1}$$

where $h(j)$ is the Dirac single-particle Hamiltonian,

$$h(j)=c\vec{\alpha}^{(j)}\cdot\vec{p}^{(j)}+\beta^{(j)}mc^2+V_n(\vec{r}_j)\,, \tag{1.2}$$

and where the Dirac $\vec{\alpha}$ and $\beta$ matrices have their usual meaning and $V_n$ is the interaction of the electron with the nucleus. This should include the finite-size effects of the nucleus and may also include the vacuum polarization by the nucleus. The two-body potential $V(i,j)$ contains the Coulomb interaction of the electrons and sometimes also contains the Breit[2] interaction, which is the $(v/c)^2$ correction to this interaction. These calculations give results which show good agreement with the experimental binding energies of the inner-shell electrons, which indicates that the underlying physics is at least close to being correct. However, Brown and Ravenhall[3] pointed out that the two-electron version of (1.1) yields no stable (normalizable) bound-state solutions. They modified (1.1) by returning to first principles, quantum electrodynamics in this case, and deriving a configuration-space Hamiltonian to replace (1.1). Their result (with a minor generalization to the case of an arbitrary number of electrons) can be written

$$H_{\mathrm{BR}}=\sum_{j=1}^{N}\Lambda_+^F(j)h(j)\Lambda_+^F(j)+\sum_{j>i=1}^{N}\Lambda_+^F(i)\Lambda_+^F(j)V(i,j)\Lambda_+^F(i)\Lambda_+^F(j)\,, \tag{1.3}$$

where the projection operation $\Lambda_+^F$ projects onto the positive-energy states of the free Dirac particles, i.e., the positive-energy states of (1.2) with $V_n=0$. This modification of the configuration-space Hamiltonian then results in stable bound states. It has been pointed out[4,5] that the free particle projection operators in (1.3) are physically reasonable when the potential $V_n$ in (1.2) is weak. (For a Coulomb approximation for $V$, this means $Z\alpha\ll 1$.) When this is not the case, the projection operators in (1.3) should more properly be replaced by $\Lambda_+^n$, which projects onto the positive-energy states of (1.2). However, in the case when the potential $V_n$ is not weak and the number of electrons in the atom is large, it is not at all clear how one should define the projection operators. In any case, the good results obtained from the use of (1.1), rather than (1.3) or its modifications, requires some explanation. This is the subject of Sec. II which may also be viewed as a more rigorous specification of the projection operators which enter into a better form of (1.3).

Section III deals with an attempt to define the elementary electron-electron interaction in the case in which $V_n$ is strong and when there are many other electrons present. Brown[6] has obtained this interaction in the case when only a few electrons are present. It, of course, reduces to

 

the Breit interaction when $V_n$ is weak but is nonlocal otherwise.

## II. DETERMINATION OF $\Lambda_+$ AND JUSTIFICATION OF NUMERICAL CALCULATIONS

The starting point for the determination of a configuration-space Hamiltonian for a many-electron atom is quantum electrodynamics,[7] which starts with the Schrödinger equation in the Fock space of electrons and photons ($\hbar = 1$),

$$\left(\frac{i\partial}{\partial t} - H_{\mathrm{QED}}\right)\Psi = 0, \tag{2.1}$$

with

$$H_{\mathrm{QED}} = H_M + H_R + H_I + H_C. \tag{2.2}$$

The Hamiltonian for the matter field alone is

$$H_M = \int d^3r\, \psi^\dagger(\vec{r}) h(\vec{r}) \psi(\vec{r}), \tag{2.3}$$

where $h$ is given by (1.2) and $\psi$ is the usual particle-wave field defined by the equal-time anticommutator

$$[\psi(\vec{r}), \psi^\dagger(\vec{r}')]_+ = \delta(\vec{r} - \vec{r}'). \tag{2.4}$$

The radiation field Hamiltonian is

$$H_R = \int \frac{d^3r}{8\pi} [\vec{E}^2(\vec{r}) + \vec{H}^2(\vec{r})], \tag{2.5}$$

where $\vec{E}$ and $\vec{H}$ are the quantized electromagnetic fields, which are defined in terms of the vector potential $\vec{A}(\vec{r})$ in the usual way. The transverse interaction Hamiltonian between the two classes of fields is

$$H_I = -\int d^3r\, \vec{j}(\vec{r}) \cdot \vec{A}(\vec{r}), \tag{2.6}$$

where the electron current is

$$\vec{j}(\vec{r}) = ec\psi^\dagger(\vec{r}) \vec{\alpha} \psi(\vec{r}). \tag{2.7}$$

The radiation gauge in which

$$\vec{\nabla} \cdot \vec{A}(\vec{r}) = 0 \tag{2.8}$$

is used here for reasons previously discussed,[6,8] and the interelectron Coulomb interaction, which is explicitly separated in this gauge, is given by

$$H_C = \tfrac{1}{2} \int d^3r\, d^3r' \psi^\dagger(\vec{r}) \psi(\vec{r}) \frac{e^2}{|\vec{r} - \vec{r}'|} \psi^\dagger(\vec{r}') \psi(\vec{r}'). \tag{2.9}$$

Finally, the electromagnetic fields are defined by the equal-time commutators

$$[E_a(\vec{r}), A_b(\vec{r}')] = \frac{ic}{2\pi^2} \int d^3k (\delta_{ab} - \hat{k}_a \hat{k}_b) e^{i\vec{k}\cdot(\vec{r} - \vec{r}')}, \tag{2.10}$$

$$[A_a(\vec{r}), \psi(\vec{r}')] = 0. \tag{2.11}$$

We are interested in states which describe an atom with no real photons present, so it is useful to partially remove the photon-matter coupling by a canonical transformation, which accomplishes this in lowest order in a series in $e^2$. The method, originally given by Schwinger,[9] will be presented in some detail in Sec. III, but it is sufficient to simply give the results here. When there are no real photons present, the most general form of the Hamiltonian is

$$\hat{H}_{\mathrm{QED}} = \hat{N} \int d^3x\, \psi^\dagger(\vec{x}) h(\vec{x}) \psi(\vec{x}) + \tfrac{1}{2} \hat{N} \int \psi^\dagger(\vec{x}_1) \psi(\vec{x}_1') V(12, 1'2') \psi^\dagger(\vec{x}_2) \psi(x_2') d^3x_1 d^3x_2 d^3x_1 d^3x_2'. \tag{2.12}$$

The normal ordering operator $\hat{N}$, occurring before the first term, is necessary in order to eliminate the difficulties associated with the Hamiltonian (1.1). The difference between this term and the same term in the absence of $\hat{N}$ is a $C$ number, which can be removed by a unitary transformation with no physical effects. (However, see the discussion at the end of this section.)

The second term in (2.12) is the two-body interaction and $V$ is the electron-electron interaction potential whose precise form will not be significant in this section. The normal ordering operator inserted before this term is done for convenience. The difference between the second term in (2.12) as it stands and the form with $\hat{N}$ absent is a sum of one-body operators and a $C$ number. These are renormalizations and radiative corrections, which are not of direct interest in this discussion and so can be dropped.

The normal ordering operator itself must now be discussed. It is usually defined with respect to the eigenfunctions of $h$, which we denote by $\phi_n(r)$ with eigenvalues $W_n$. In that case the field operators are expanded as

$$\psi(\vec{r}) = \sum_n \phi_n(\vec{r}) b_n, \tag{2.13}$$

where

$$[b_n, b_{n'}^\dagger]_+ = \delta_{nn'}. \tag{2.14}$$

The operators $b_n$ are interpreted as destruction operators when $W_n > 0$, and creation operators when $W_n < 0$. This is made explicit by their action on the particle vacuum state $|0\rangle$, given by

$$b_n|0\rangle = 0, \quad W_n > 0$$
$$b_n^\dagger|0\rangle = 0, \quad W_n < 0. \tag{2.15}$$

The normal ordering of the first term of (2.12) then results in

$$\hat{N}\int d^3x\, \psi^\dagger(\vec{x})h(\vec{x})\psi(\vec{x}) = \sum_n^{(+)} W_n b_n^\dagger b_n + \sum_n^{(-)} |W_n| b_n b_n^\dagger, \tag{2.16}$$

where the superscripts on the sums refer to the sign of the eigenvalues $W_n$. We shall allow for a more general form of the normal ordering operator by introducing a more general set of states in (2.13), which are eigenfunctions of a single-particle operator, which we shall write as

$$\bar{h} = h + \Omega, \tag{2.17}$$

where $\Omega$ is to be specified later. In that case the normal ordering becomes

$$\hat{N}\int d^3x\, \psi^\dagger h\psi = \int [\psi^\dagger(\Lambda_+ h\Lambda_+ + \Lambda_+ h\Lambda_- + \Lambda_- h\Lambda_+)\psi - \psi(\Lambda_- h\Lambda_-)_t\psi^\dagger](dx), \tag{2.18}$$

where the subscript $t$ in the last term indicates the transposed form of the operator. The projection operator $\Lambda_+$ projects onto the positive-energy states of $\bar{h}$ [Eq. (2.17)]. The vacuum is also redefined so that (2.15) becomes

$$\Lambda_+\psi|0\rangle = \psi^\dagger\Lambda_-|0\rangle = 0. \tag{2.19}$$

The usual normal ordering of the first term of (2.12), which is (2.16), is a positive definite operator and the more general form (2.18) is not necessarily so, but it can be shown to be bounded from below, which is a sufficient condition to remove the difficulties associated with (1.1).

The Fock-space Hamiltonian can be used to generate a configuration-space Hamiltonian with the aid of the Rayleigh-Ritz variational principle. We must first assume a form for the Fock-space wave function which satisfies (2.1). It is known that the state which describes a system of electrons of total charge $(-Ne)$ will have a leading term with $N$ electrons. The second term will contain $(N+1)$ electrons plus one positron and succeeding terms will have additional pairs. The mathematics becomes too complicated to include anything but the first term, so we must drop all virtual pairs from this description. The wave function is then approximated by the term with no virtual pairs and is written

$$\Psi \simeq e^{-iEt}\Phi = e^{-iEt}\int (dx_1)\cdots(dx_N)\psi^\dagger(1)\cdots\psi^\dagger(N)\Lambda_+'(1)\cdots\Lambda_+'(N)\chi'(1\cdots N)|0\rangle, \tag{2.20}$$

where we have, for the moment, allowed a different projection operator $\Lambda_+'$ in (2.20) than that defined by (2.17) and the associated discussion. This is clearly redundant because of the second part of (2.19). That is, (2.19) allows us to write

$$\psi^\dagger(j)|0\rangle = \psi^\dagger(j)\Lambda_+(j)|0\rangle,$$

so that the projection operator $\Lambda_+(1)\cdots\Lambda_+(N)$ can be inserted immediately to the right of $\psi^\dagger(1)\cdots\psi^\dagger(N)$ in (2.20). Then the product $\Lambda_+'(1)\cdots\Lambda_+'(N)\chi'(1\cdots N)$ can be identified as a new wave function $\chi(1\cdots N)$, and so the allowance for the difference between the projection operators $\Lambda_+(j)$ and $\Lambda_+'(j)$ is redundant. We therefore rewrite (2.20) as

$$\Psi \simeq e^{-iEt}\Phi = e^{-iEt}\int (dx_1)\cdots(dx_N)\psi^\dagger(1)\cdots\psi^\dagger(N)\Lambda_+(1)\cdots\Lambda_+(N)\chi(1\cdots N)|0\rangle, \tag{2.21}$$

where $\Lambda_+$ is defined by (2.17) with $\Omega$ to be determined below. The function $\chi(1\cdots N)$ will then be interpreted as the $N$-electron configuration-space wave function of the atom.

The Rayleigh-Ritz principle can now be used in the form

$$E = \frac{[\Phi, \hat{H}_{\mathrm{QED}}\Phi]}{[\Phi,\Phi]} = \frac{(\chi, H_{\mathrm{cs}}\chi)}{(\chi,\chi)}, \tag{2.22}$$

where [ , ] is an inner production in Fock space and ( , ) is an inner product in configuration space. The transition to the second form of (2.22) must be taken with a little care. (This is discussed in the Appendix.) The fact that the definition of the vacuum is (2.19), rather than (2.15), simplifies the process with the result

$$H_{\mathrm{cs}} = \sum_{j=1}^{N}\Lambda_+(j)h(j)\Lambda_+(j) + \sum_{i>j}^{N}\Lambda_+(i)\Lambda_+(j)V(i,j)\Lambda_+(i)\Lambda_+(j), \tag{2.23}$$

where $V$ is the two-body interaction potential in (2.12). Variation of (2.22) with respect to $\chi$ yields the Schrödinger equation in configuration space

$$(E-H_{cs})\chi=0\,, \tag{2.24}$$

where the configuration-space Hamiltonian is given by (2.23). The projection operator $\Lambda_+$ is still undetermined since $\Omega$ in (2.17) has not been specified, but variation of $E$ with respect to $\Omega$ can yield an equation which will determine it. To that end we may rewrite (2.22) as

$$\frac{E}{N}=\frac{(\chi,[\Lambda_+(1)h(1)\Lambda_+(1)+\frac{1}{2}(N-1)\Lambda_+(1)\Lambda_+(2)V(1,2)\Lambda_+(1)\Lambda_+(2)]\chi)}{(\chi,\chi)} \tag{2.25}$$

and define density matrices from the wave function $\chi$,

$$\begin{aligned}\rho_2(\vec{r}_1\vec{r}_2;\,\vec{r}_1'\vec{r}_2')&=\int d^3r_3\cdots d^3r_N\chi(\vec{r}_1\vec{r}_2\vec{r}_3\cdots\vec{r}_N)\chi^*(\vec{r}_1'\vec{r}_2'\vec{r}_3\cdots\vec{r}_N)\,,\\ \rho_1(\vec{r}_1,\vec{r}_1')&=\int d^3r_2\rho_2(\vec{r}_1\vec{r}_2;\,\vec{r}_1'\vec{r}_2)\,,\end{aligned} \tag{2.26}$$

with the normalization

$$\int d^3r_1\rho_1(\vec{r}_1,\vec{r}_1)=1\,. \tag{2.27}$$

Then (2.25) can be rewritten as

$$\frac{E}{N}=\mathrm{tr}_1\rho_1(1)\Lambda_+(1)h(1)\Lambda_+(1)+\tfrac{1}{2}(N-1)\,\mathrm{tr}_{12}\rho_2(12)\Lambda_+(1)\Lambda_+(2)V(12)\Lambda_+(1)\Lambda_+(2)\,, \tag{2.28}$$

where the notation $\mathrm{tr}_{12}$ means a trace over coordinates 1 and 2. The variation of $E$ with respect to $\Omega$ is accomplished by variation of only $\Lambda_+$ since $\chi$, and therefore $\rho_1$ and $\rho_2$, are independently varied. This variation is accomplished with the use of[4]

$$\delta\Lambda_+=\Lambda_-Q\Lambda_++\Lambda_+Q^\dagger\Lambda_-\,, \tag{2.29}$$

where $\Lambda_-=1-\Lambda_+$ and

$$Q=\int_0^\infty dv\,e^{\bar{h}v}\delta\Omega e^{-\bar{h}v}\,. \tag{2.30}$$

The variation of (2.25) then yields

$$0=\mathrm{tr}_1\rho_1(1)[Q^\dagger(1)\Lambda_-(1)h(1)+h(1)\Lambda_-(1)Q(1)]+(N-1)\,\mathrm{tr}_{12}\rho_2(12)[Q^\dagger(1)\Lambda_-(1)V(12)+V(12)\Lambda_-(1)Q(1)]\,, \tag{2.31}$$

where use has been made of the fact that $\Lambda_-$ acting on either $\rho_1$ or $\rho_2$ vanishes. This comes from the definitions (2.26) and the Schrödinger equation (2.24) with (2.20). Use has also been made of the symmetry of $\rho(12)$ and $V(12)$ in their arguments. The use of (2.30) in (2.31) results in

$$\begin{aligned}0=&\int_0^\infty dv\,\mathrm{tr}_1\delta\Omega(1)[e^{\bar{h}(1)v}\Lambda_-(1)h(1)\rho_1(1)e^{-\bar{h}(1)v}+e^{-\bar{h}(1)v}\rho_1(1)h(1)\Lambda_-(1)e^{\bar{h}(1)v}]\\&+\int_0^\infty dv\,\mathrm{tr}_{12}\delta\Omega(1)[e^{\bar{h}(1)v}\Lambda_-(1)V(12)\rho_2(12)e^{-\bar{h}(1)v}+e^{-\bar{h}(1)v}\rho_2(12)V(12)\Lambda_-(1)e^{\bar{h}(1)v}]\,,\end{aligned}$$

and use is now made of the fact that $\delta\Omega(1)$ is an arbitrary infinitesimal operator to yield an equation to determine $\Omega$. We also use

$$\rho(1)h(1)\Lambda_-(1)=-\rho(1)\Omega(1)\Lambda_-(1) \tag{2.33}$$

and its Hermitian conjugate in the first term of (2.32). The result is

$$\begin{aligned}0=\int_0^\infty dv\{&e^{\bar{h}(1)v}\Lambda_-(1)[-\Omega(1)\rho_1(1)+(N-1)\,\mathrm{tr}_2V(12)\rho_2(12)]e^{-\bar{h}(1)v}\\&+e^{-\bar{h}(1)v}[-\rho_1(1)\Omega(1)+(N-1)\,\mathrm{tr}_2\rho_2(12)V(12)]\Lambda_-(1)e^{\bar{h}(1)v}\}\,.\end{aligned} \tag{2.34}$$

If we operate from the left with $\Lambda_-$ and from the right with $\Lambda_+$, the last term vanishes. We may then form

the $(q|\cdots|n)$ matrix element of the remaining part, where $(q|$ is a negative-energy eigenstate of $\bar{h}$ and $|n)$ is a positive-energy eigenstate. The $v$ integral may then be performed with the result

$$\frac{1}{|W_q|+W_n}(q|-\Omega(1)\rho_1(1)+(N-1)\,\mathrm{tr}_2 V(12)\rho_2(12)|n)=0\,,$$

which can be written as

$$\Omega(1)\rho_1(1)=(N-1)\,\mathrm{tr}_2 V(12)\rho_2(12)\,, \tag{2.35}$$

where the $(-|\cdots|+)$ matrix element, in a representation of the states of $\bar{h}$, is understood. [The Hermitian conjugate of (2.33) is also true.] This equation determines $\Omega$ in a very complex way since $\Omega$ enters into $\Lambda_+$ and therefore into $\chi$, which in turn determines $\rho_1$ and $\rho_2$.

An exact solution of (2.35) is a hopeless task, but if $\chi$ is approximated by a Hartree-Fock solution, then $\rho_1$ and $\rho_2$ can be written as

$$\begin{aligned}\rho_1(\vec{r}_1;\vec{r}_1')&=\frac{1}{N}\sum_{j=1}^{N}W_j(\vec{r}_1)W_j^*(\vec{r}_1')\,,\\ \rho_2(\vec{r}_1\vec{r}_2;\vec{r}_1'\vec{r}_2')&=\frac{1}{N(N-1)}\sum_{i,j=1}^{N}W_i(\vec{r}_1)W_j(\vec{r}_2)[W_i(\vec{r}_1')W_j(\vec{r}_2')-W_j(\vec{r}_1')W_i(\vec{r}_2')]^*\,,\end{aligned} \tag{2.36}$$

where the $W_i$ are the Hartree-Fock single-particle orbitals based upon the $N$-electron Hamiltonian (2.23). Substitution of (2.36) into (2.35), and the formation of the $(q|\cdots|n)$ matrix element in the *Hartree-Fock* representation yields

$$\sum_{j=1}^{N}(q|\Omega|n)\delta_{n,j}=\sum_{j;1}^{N}[(qj|V|ij)\delta_{n,i}-(qi|V|ij)\delta_{n,j}]\,. \tag{2.37}$$

If $n$ is not one of the occupied orbitals then this yields no information but, if it is, then this becomes

$$(q|\Omega|n)=\sum_{j=1}^{N}[(qj|V|nj)-(qj|V|jn)]\,. \tag{2.38}$$

It should be pointed out that (2.35) was derived with the understanding that it applies only for the $(-|\,|+)$ matrix element in a single-particle representation defined by the Hamiltonian $\bar{h}$. In obtaining (2.38) we used a $(-|\;\;|+)$ matrix element in the Hartree-Fock single-particle representation, but the result shows that these representations are the same, since the right-hand side of (2.38) is precisely the $(-|\;\;|+)$ matrix element of the Hartree-Fock potential. This is a direct demonstration that the $(-|\cdots|+)$ matrix element of $\Omega$ is the same as the $(-|\cdots|+)$ matrix element of the Hartree-Fock potential obtained from the many-body Hamiltonian (2.23). It also implies the same thing for the $(+|\cdots|+)$ and $(-|\cdots|-)$ matrix elements, since (2.38) also shows that the eigenstates of $\bar{h}$ [Eq. (2.17)] must be identical with the Hartree-Fock orbitals $W_j$ in (2.36). Hence, $\Omega$ is the Hartree-Fock potential when the Hartree-Fock approximation is made for the wave function $\chi$.

We now return to the problem of the numerical calculations raised in the Introduction. All of these are Hartree-Fock calculations based upon the Hamiltonian (1.1). They all operate with the implicit constraint that only positive-energy single-particle states will be retained. In effect this inserts the operators $\Lambda_+^{HF}$ in place of the $\Lambda_+^F$, which occur in (1.3), where $\Lambda_+^{HF}$ projects onto the positive-energy states of $\bar{h}$ with $\Omega$ replaced by $\Omega^{HF}$. But we have shown that this is a correct prescription when the simplifying assumption (2.36) is made. This provides an understanding of the agreement of numerical calculations with experiment. A minor point of concern can, however, be raised with regard to the use of (1.1) in a Hartree-Fock calculation with only the implicit appearance of $\Lambda_+^{HF}$. It is possible to generate incorrect results in this way by an iteration method for solving the equation, since negative-energy states can intrude as intermediate states (where they do not belong) with this method. For example, suppose that (1.1) is used as a starting point, and that $V(i,j)$ is taken to be the Coulomb plus the Breit interaction. If $Z$ is not too large, it is reasonable to treat the Breit interaction as a perturbation. Then the zero-order problem would be (1.1) with only the Coulomb electron-electron interaction. If this is treated by an analytic Hartree-Fock technique with an implicit constraint of positive-energy orbitals, the result is a set of Hartree-Fock orbitals which is almost identical with those which would have emerged from the Hartree-Fock treatment of the more correct form, (2.23). Now suppose that the effect of the Breit interaction is included. Its first-or-

der effect is obtained from first-order perturbation theory using the Hartree-Fock orbitals described above. The result is correct. However, the second-order contribution of the Breit interaction would introduce negative-energy intermediate states, and it is well known[10] that this gives a large and incorrect result. This is a simple example of the possibility of an iterative technique in which the Hamiltonian (1.1) gives wrong results.

In the limit of only a few electrons ($N \ll Z$), the potential (2.38) becomes small compared to the nuclear potential and the projection operators in $H_{cs}$ [Eq. (2.23)] can be replaced by $\Lambda_+^n$ in which $\Omega$ is set equal to zero. In the further limit in which the nuclear potential is small, $\Lambda_+$ can be replaced by $\Lambda_+^F$ and the Brown and Ravenhall[3] result, (1.3), is recovered.

The normal ordering described above results in additive $C$ numbers in the Hamiltonian, which are discarded on the usual grounds that $C$ numbers have no physical effects in a field theory. However, the $C$ number, which has been discarded here, depends upon the state of the system, since $\Omega$ and consequently $\Lambda_+$ are state dependent. This means that the vacuum is state dependent and therefore, so is the $C$ number, which we discard. This does indeed cause conceptual difficulties in a more exact theory than is contemplated here.[11]

Recently, Sucher[5] discussed the Hartree-Fock reduction of Hamiltonians such as (1.3). He points out that the implicit constraint of retaining only positive-energy orbitals results in only small errors in the single-particle energies for small values of $Z\alpha$. The reason is that $\Lambda_+^n$ or $\Lambda_+^F$ differ from unity by only small amounts when acting on the basically nonrelativistic Hartree-Fock orbitals. The development given above goes even further: The Hartree-Fock reduction of (1.1) results in *exactly the same* single-particle energies as the Hartree-Fock reduction of the more correct Hamiltonian, (1.3) with $\Lambda_+^F$ replaced by $\Lambda_+^{HF}$.

## III. THE ELEMENTARY TWO-ELECTRON INTERACTION

The usual method,[9] used for the approximate decoupling of the matter and radiation field, involves a series of unitary transformations from the Schrödinger to the interaction representation and back. They can be condensed[4] to a single unitary transformation of the form

$$\Psi = e^{-i\sigma}\Psi', \tag{3.1}$$

where

$$\sigma = -\tfrac{1}{2}\int_{-\infty}^{\infty} d\tau H_I(\tau)\epsilon(\tau), \tag{3.2}$$

$$\epsilon(I) = \mathrm{sgn}(\tau), \tag{3.3}$$

and

$$H_I(\tau) = e^{iH_0\tau}H_I e^{-iH_0\tau}. \tag{3.4}$$

$H_I$ is the coupling between matter and transverse photons [Eq. (2.6)] and $H_0$ is usually taken to be the "zero-order Hamiltonian" $H_M + H_c$. This transformation, as we shall see, yields an infinite series of terms for the Hamiltonian. The lowest two-electron term has intermediate states, in which the propagation of the electrons is defined by $H_0$. In the usual case, they then propagate in single-particle eigenstates of $h$ [Eq. (1.2)]. This would seem to be inappropriate for the many-electron case where $H_c$ [Eq. (2.9)] is expected to be as important as $V_n$. We therefore generalize the usual method so that

$$H_0 = H_M + H_R + H_C. \tag{3.5}$$

The unitary transformation defined by (3.1)–(3.5) then generates a new Hamiltonian of the form

$$H = H_M + H_R + \sum_{n=0}^{\infty}\frac{i^n}{n!}C_n[\sigma,H_C] + \sum_{n=1}^{\infty}\frac{i^n n}{(n+1)}C_n[\sigma,H_I], \tag{3.6}$$

where $C_n$ is defined by

$$C_n[\sigma,H] = [\sigma,C_{n-1}[\sigma,H]],$$
$$C_0[\sigma,H] = H. \tag{3.7}$$

The series in the last two terms of (3.6) are expansions in powers of $H_I$, which is an expansion in the number of transverse photons exchanged. If we first consider the Coulomb contribution, it is

$$H_C + [\sigma,H_C] + \frac{i^2}{2}[\sigma,[\sigma,H_C]] + \cdots. \tag{3.8}$$

The first term is the Coulomb part of the electron-electron interaction and will be retained. The second term is an interference between Coulomb and transverse terms, which is of the order $e^3$ and off diagonal in the photon number. Its lowest contribution to a potential comes from its appearance in the second order, which is of the order $e^6$, and so it is dropped here. The third term is of the order $e^4$, diagonal in the photon number, and it contains three-body potentials[12] as well as radiative corrections to the two-body potentials. It is too small to be included here. Subsequent terms of the series are dropped for the same reason.

The last term of (3.6) is the purely transverse part of the interaction. The first few terms are

$$\frac{i}{2}[\sigma,H_I] + \frac{i^2}{3}[\sigma,[\sigma,H_I]] + \frac{i^3}{8}[\sigma,[\sigma,H_I]] + \cdots. \tag{3.9}$$

The first term is the one-photon part of the transverse interaction, which will be considered below. The remaining terms of the series are dropped for reasons similar to those given for higher terms of (3.8).

The leading transverse interaction is

$$\frac{i}{2}[\sigma,H_I]=-\frac{i}{4}\int d\tau\epsilon(\tau)[H_I(\tau),H_I]$$

$$=-\frac{i}{8}\int d^3r\,d^3r'd\tau\epsilon(\tau)[j_a(\vec{r},\tau),j_b(\vec{r}')]_+[A_a(\vec{r},\tau),A_b(\vec{r}')]+[j_a(\vec{r},\tau),j_b(\vec{r}')][A_a(\vec{r},\tau),A_b(\vec{r}')]_+\}\,, \tag{3.10}$$

where

$$A_a(\vec{r},\tau)=e^{iH_R\tau}A_a(\vec{r})e^{-iH_R\tau} \tag{3.11}$$

and

$$j_a(\vec{r},\tau)=e^{i(H_M+H_C)\tau}j_a(\vec{r})e^{-i(H_M+H_C)\tau}\,. \tag{3.12}$$

The new feature of this interaction is the appearance of $H_C$ in the exponents of (3.12). Without it, $j_a(\vec{r},\tau)$ would be a single-particle operator and the commutator $[j_a,j_b]$, in the last term of (3.10), would also be a single-particle operator of the order $e^2$, and so negligible compared to $V_n$. However, $j_a$ is a many-body operator due to the correlations induced by $H_C$, and this commutator is also a many-body operator for this reason.

Exact evaluation of the time evolution operators in (3.12) is equivalent to a solution of the many-body problem with the Hamiltonian $H_M+H_C$, which is beyond our current capabilities. It can be approximated by an optimized single-particle form, which is the Hartree-Fock Hamiltonian. In order to do this, we must solve a Hartree-Fock problem for $N$ electrons with the starting Hamiltonian

$$H'=\hat{N}H_M+H_C\,, \tag{3.13}$$

where the normal ordering of the first term appears here as it did in (2.12). The reduction of (3.13) to its Hartree-Fock approximation can be performed in exactly the same manner as was given in the preceding section. The result is a set of orbitals and eigenvalues, which we call $w_n(\mathrm{CH})$ and $W_n(\mathrm{CH})$, respectively, the CH indicating that the input two-body interaction is Coulomb and it is treated by a Hartree-Fock reduction. If $h_{\mathrm{CH}}$ is the (nonlocal) one-body Hamiltonian for these, then

$$(W_n(\mathrm{CH})-h_{\mathrm{CH}})w_n(\mathrm{CH})=0\,, \tag{3.14}$$

and $H$ can be approximated by a single-particle Fock-space Hamiltonian given by

$$H'_{\mathrm{HF}}=\hat{N}\int d^3r\,d^3r'\psi^\dagger(\vec{r})h_{\mathrm{CH}}(\vec{r},\vec{r}')\psi(\vec{r}')$$

$$=\hat{N}\sum_n W_n(\mathrm{CH})b_n^\dagger(\mathrm{CH})b_n(\mathrm{CH})\,, \tag{3.15}$$

where

$$b_n(\mathrm{CH})=\int d^3r\,w_n^*(\mathrm{CH},\vec{r})\psi(\vec{r})\,. \tag{3.16}$$

With this approximation the last term of (3.10) is a one-electron potential of the order $e^2$ and so is dropped relative to $V_n$. The first term of (3.10) is retained, and its form is only slightly changed from the elementary transverse interactions previously[4-6] discussed. The one change is that the electrons propagate in intermediate states under the influence of the single-particle Hamiltonian $h_{\mathrm{CH}}$ instead of $h$ [Eq. (1.2)]. The result can then be written by simply making this transcription. The first term of (3.10) can then be written

$$H_T=-\tfrac{1}{2}\{\psi^\dagger(1)\psi^\dagger(2),[\eta(12)+\eta(21)]\psi(2)\psi(1)\}\,, \tag{3.17}$$

where

$$\eta(12)=\frac{ie^2}{4}\int d\tau\,\epsilon(\tau)e^{ih_{\mathrm{CH}}(1)\tau}\alpha_a^{(1)}$$

$$\times D_{ab}(\vec{r}_{12},(\tau)\alpha_b^{(2)}e^{-ih_{\mathrm{CH}}(1)\tau}\,, \tag{3.18}$$

where the $D$ function is the commutator of the $A$'s and is given by[9]

$$D_{ab}(\vec{r},\tau)=-\frac{ic}{2\pi^2}\int\frac{d^3k}{k}(\delta_{ab}-\hat{k}_a\hat{k}_b)e^{(\vec{k}\cdot\vec{r})}\sin ck\tau\,. \tag{3.19}$$

Explicit use of (3.19) in (3.18) results in another form

$$\eta_{n_1,n'_1}=\frac{e^2}{4}\int d^3r_1d^3r_2\phi_n^*(\vec{r}_1)\alpha_a^{(1)}\phi_{n'}(\vec{r}_1)\phi_l^*(\vec{r}_2)\alpha_b^{(2)}\phi_{l'}(\vec{r}_2)(\delta_{ab}\nabla^2-\nabla_a\nabla_b)r_{12}\left(\frac{2c}{W_{nn'}(\mathrm{CH})}r_{12}\sin\frac{W_{nn'}(\mathrm{CH})r_{12}}{2c}\right)^2\,, \tag{3.20}$$

where $W_{nn'}(\mathrm{CH})=W_n(\mathrm{CH})-W_{n'}(\mathrm{CH})$ and the $\phi_n$ are eigenfunctions of $\bar{h}$ [Eq. (2.17)]. Finally, the elementary two-body interaction in (2.13) is specified by

$$V_{n_1,n'_1}=C_{n_1,n'_1}-\eta_{n_1,n'_1}-\eta_{l_n,l'_{n'}}\,, \tag{3.21}$$

where the Coulomb matrix element arises from the first term of (3.8) and is

$$C_{nl,n'l'}=\left(\phi_n(1)\phi_l(2),\frac{e^2}{r_{12}}\phi_{n'}(1)\phi_{l'}(2)\right). \tag{3.22}$$

The Hamiltonian specified above presents a lengthy calculational task necessary to extract numerical results. One first has to obtain the Hartree-Fock states and energies for the $N$-electron problem with only the Coulomb interaction among the electrons, (3.13). These then must be used to construct the elementary transverse two-body interaction (3.20), which are then inserted in the total two-body interaction (3.21). This can then be substituted back into (2.23) to get the configuration-space Hamiltonian, which usually must also be treated by a Hartree-Fock reduction. A simplification of this procedure is available, which will probably not change the results significantly. The idea is that $\eta$ is only significant when coupling relativistic electrons. These are the inner ones for which the dominant potential is the nuclear potential with the screening, due to $\Omega$, playing a lesser role. Therefore, it should not make much difference if $h_{CH}$ in the intermediate state in (3.18) is replaced by the single-particle (Hartree-Fock) Hamiltonian based upon the full two-body interaction (3.21), rather than just the Coulomb interaction. This would replace the $W_{nn'}$(CH) by the full single-particle energies. The result would be a single nonlinear eigenvalue problem instead of the process described above which is that of two linear eigenvalue problems. The nonlinear problem yields an equation of the form

$$W_n(\mathrm{HF})\delta_{nn'}-(n|h|n')-\sum_{j=1}^{N}\left(n'j\left|\frac{e^2}{r_{12}}-\frac{e^2}{4}[f(W_{nn'}(\mathrm{HF}),\vec{r}_{12})+f(0,\vec{r}_{12})]\right|nj\right)$$
$$+\sum_{j=1}^{N}\left(n'j\left|\frac{e^2}{r_{12}}-\frac{e^2}{4}[f(W_{n'j}(\mathrm{HF}),\vec{r}_{12})+f(W_{jn}(\mathrm{HF}),\vec{r}_{12})]\right|jn\right)=0, \tag{3.23}$$

where

$$f(W_1\vec{r}_{12})=(\vec{\alpha}^{(1)}\cdot\vec{\alpha}^{(2)}\nabla^2-\vec{\alpha}^{(1)}\cdot\vec{\nabla}\vec{\alpha}^{(2)}\cdot\vec{\nabla})r_{12}\left(\frac{2c}{Wr_{12}}\sin\frac{Wr_{12}}{2c}\right)^2. \tag{3.24}$$

The basic functions appearing here are $w_n$(HF), the final Hartree-Fock orbitals. From (3.24) it is evident that the appearance of the eigenvalues $W_n$(HF) in the potentials is a relativistic correction. In lowest order, $(c\to\infty)$, these give the Breit interaction, and it is clear that further corrections will only be significant for the inner orbitals. This will be discussed in a subsequent publication.

## ACKNOWLEDGMENTS

This research was supported by U.S.O.N.R. Contract No. N00014-76C-0014, NASA Grant No. NSG 5334, and CUNY Faculty Research Award No. 13098.

## APPENDIX

The transition from the Fock space to the configuration-space form of (2.22) will be discussed here. The starting point, $\hat{H}_{\mathrm{QED}}$, is given in (2.12) and the state vector $\Phi$ in (2.21). The definition of the vacuum [Eq. (2.19)] is based upon the projection operators $\Lambda_+$, which in turn are based upon the Hamiltonian $\bar{h}$ [Eq. (2.17)]. The normal ordering operator $\hat{N}$ in $H_{\mathrm{QED}}$, [Eq. (2.12)], is also defined with respect to this single-particle Hamiltonian. This makes the calculation much simpler. For example, the one-body part of (2.12) will contribute to (2.22) a term

$$\int dy_1\cdots dy_n dz_1\cdots dz_n dx\,\chi^*(y_1\cdots y_n)\Lambda_+(y_1)\cdots\Lambda_+(y_n)\langle 0|\psi(y_1)\cdots\psi(y_n)\hat{N}[\psi^\dagger(x)h(x)\psi(x)]\psi^\dagger(z_n)\cdots\psi^\dagger(z_1)|0\rangle$$
$$\times\Lambda_+(z_n)\cdots\Lambda_+(z_1)\chi(z_1\cdots z_n). \tag{A1}$$

The $\psi^\dagger(z_i)$ are all creation operators because of the appearance of $\Lambda_+(z_i)$ and (2.19). The negative-energy part of $\psi(x)$ anticommutes with these and gives no contribution to (A1) because of the normal ordering [Eq. (2.18)]. The positive-energy part of $\psi(x)$, which annihilates the vacuum, (2.19), can also be moved to the right through the $\psi^\dagger(z_i)$ with the use of (2.4), and it is the delta functions of (2.4) which gives the nonvanishing contribution. Thus,

$$\psi(x)\psi^\dagger(z_N)\cdots\psi^\dagger(z_1)|0\rangle=\sum_{j=1}^{N}\delta(x-z_j)(-1)^{j+1}\psi^\dagger(z_N)\cdots\hat{j}\cdots\psi^\dagger(z_1)|0\rangle, \tag{A2}$$

where the notation $\hat{j}$ means that $\psi^\dagger(z_j)$ is to be omitted from the product. This equation is understood to

apply only to the positive-energy components of all of the operators and this is exactly what occurs in (A1). The left-hand side of (A1),

$$\langle 0|\psi(y_1)\cdots\psi(y_N)\psi^\dagger(x)\,,$$

can be evaluated as the Hermitian conjugate of a form such as (A2). When this and (A2) are combined we may use

$$\langle 0|\psi(y_1)\cdots\psi(y_N)\psi^\dagger(z_N)\cdots\psi^\dagger(z_1)|0\rangle = \det|\delta(y_i - z_j)|\,, \tag{A3}$$

where the left-hand side of (A3) is an $N\times N$ determinant, each of whose entries is a delta function. The use of the fact that $\chi$ must be antisymmetric, in any pair of its arguments, gives the result that this term is

$$N!\left(\chi^*(1\cdots N)\Lambda_+(1)\cdots\Lambda_+(N)\sum_{j=1}^{N}h(j)\Lambda_+(1)\cdots\Lambda_+(N)\chi(1\cdots N)\right). \tag{A4}$$

In a similar fashion, the normalization inner product can be evaluated with the result

$$[\Phi,\Phi] = N!\,(\chi,\chi)\,. \tag{A5}$$

This yields a contribution

$$\Lambda_+(1)\cdots\Lambda_+(N)\sum_{j=1}^{N}h(j)\Lambda_+(1)\cdots\Lambda_+(N) \tag{A6}$$

for the first term of the configuration-space Hamiltonian, (2.23). A similar analysis yields

$$\Lambda_+(1)\cdots\Lambda_+(N)\sum_{i>j=1}^{N}V(1,j)\Lambda_+(1)\cdots\Lambda_+(N) \tag{A7}$$

for the second. The sum of these two is slightly more complicated than (2.23). However, it can be simplified with the result (2.23) by the use of

$$\Lambda_+(j)\chi_+(1\cdots N) = 0\,,\quad j = 1\cdots N \tag{A8}$$

which is a direct consequence of the Schrödinger equation (2.24).

---

*Permanent address: Physics Department, The City College of the City University of New York, New York, N. Y. 10031.

[1]I. Lindgren and A. Rosen, Case Stud. At. Phys. 4, 93 (1974); I. P. Grant, Adv. Phys. 19, 747 (1970); J. B. Mann and W. R. Johnson, Phys. Rev. A 4, 41 (1971).
[2]G. Breit, Phys. Rev. 39, 616 (1932).
[3]G. E. Brown and D. G. Ravenhall, Proc. R. Soc. London Ser. A 208, 532 (1951).
[4]M. H. Mittleman, Phys. Rev. A 5, 2395 (1972).
[5]J. Sucher, Phys. Rev. A 22, 348 (1980).
[6]G. E. Brown, Philos. Mag. 43, 467 (1952).
[7]See, for example, J. Sakuri, *Advanced Quantum Mechanics* (Addison-Wesley, Reading, Mass., 1967).
[8]Y. Nambu, Prog. Theor. Phys. 5, 614 (1950).
[9]J. Schwinger, Phys. Rev. 74, 1439 (1948).
[10]H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic, New York, 1959), p. 198.
[11]I am indebted to Professor F. Coester for pointing out this difficulty to me. The problem has also been raised in the nuclear context by S. A. Chin, Ann. Phys. (N.Y.) 108, 301 (1977).
[12]H. Promakoff and T. Holstein, Phys. Rev. 55, 218 (1938); C. Chanmugam and S. S. Schweber, Phys. Rev. A 1, 1369 (1970); M. H. Mittleman, *ibid.* 4, 893 (1971).