Foundations of the relativistic theory of many-electron atoms

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The many-electron Dirac-Coulomb Hamiltonian H_{DC}, on which most calculations of relativistic effects in many-electron atoms are based, has no normalizable eigenfunctions corresponding to atomic bound states. Two alternative Hamiltonians H_+ and h_+, which are derivable within the framework of quantum electrodynamics and hence do not suffer from this defect, are considered. They differ from H_{DC} by the presence of external-field or free positive-energy projection operators in the interaction terms; the Breit operator can be included in H_+ or h_+ without any difficulty arising thereby. The use of H_+ or h_+ as a starting point for a systematic approach to the calculation of energy levels and transition amplitudes in atomic physics is described. Hartree-Fock (HF) approximations to the eigenfunctions of H_+ and h_+ are defined and the related relativistic HF equations are derived. The results are used to clarify the meaning of the solutions of the Dirac-Hartree-Fock (DHF) equations associated with H_{DC}. The reduction of H_+ and h_+ to fully equivalent relativistic Schrödinger-Pauli Hamiltonians H_P^{rel} and h_P^{rel} is carried out in closed form. The HF equations associated with h_P^{rel} are found to be simpler than the DHF equations.

I. INTRODUCTION

Interest in the relativistic aspects of many-electron atoms has increased greatly in the past decade. A popular approach to the problem of taking relativistic effects into account has been based on a relativistic version of the Hartree-Fock (HF) approximation, the so-called Dirac-Hartree-Fock (DHF) approximation.[1] In this approach an N-electron wave function $\chi = \chi(1,2,\ldots,N)$ is constructed as a Slater determinant of one-electron Dirac orbitals $\chi_i(\vec{r})\,(i=1,\ldots,N)$, determined from the variational principle

$$\delta\langle\chi|\mathcal{H}_{DC}|\chi\rangle = 0\,. \tag{1.1}$$

Here $\mathcal{H}_{DC}$ is the Dirac-Coulomb Hamiltonian defined by

$$\mathcal{H}_{DC} = \sum_{i=1}^{N} \mathcal{H}_{D;ext}(i) + V_{ee}\,, \tag{1.2}$$

with $\mathcal{H}_{D;ext}(i)$ the Dirac Hamiltonian for one electron in an external field with four-potential $A^{\mu}_{ext}(\vec{r})$

$$\mathcal{H}_{D;ext}(i) = \vec{\alpha}_i\cdot\vec{p}_i + \beta_i m - eA^0_{ext}(\vec{r}_i) + e\vec{\alpha}_i\cdot\vec{A}_{ext}(\vec{r}_i) \tag{1.3}$$

and V_{ee} the sum of electron-electron Coulomb interactions,

$$V_{ee} = \sum_{i<j} e^2/r_{ij}\,. \tag{1.4}$$

The resulting equations for the χ_i, the DHF equations, are then solved numerically and yield a relativistic HF wave function, χ^{HF}, for a low-lying state of the atom. The DHF equations reduce to the ordinary HF equations in the nonrelativistic limit ($\alpha Z \ll 1$) and χ^{HF} reduces to an HF approximation φ^{HF} for the nonrelativistic wave function φ. So all seems well at first sight.

However, it has been known for a long time that the operator $\mathcal{H}_{DC}$ has no eigenfunctions corresponding to bound states. The reason is that any normalizable eigenstate $\psi_n^{(0)}$ of

$$\mathcal{H}_{DC}^{(0)} = \sum_i \mathcal{H}_{D;ext}(i)$$

lies embedded in a sea of non-normalizable product states with the same total energy, in which, e.g., one electron is in a continuum state with positive energy $E_1 > m$ and another is in a continuum state with negative energy $E_2 < -m$ (Ref. 2). The switching on of V_{ee} will cause $\psi_n^{(0)}$ to "dissolve into the continuum," to use a language familiar from the description of autoionization. In view of this, a number of questions may be raised. (i) Granted that χ^{HF} is an "approximate wave function," to what wave function is it an approximation? (ii) Is there a physically sensible relativistic N-electron Hamiltonian $\mathcal{H}$ which takes the most important effects of the electron-electron interaction into account and which has bound-state eigenfunctions? (iii) If so, can $\mathcal{H}$ serve both as a starting point for a practical central-field approximation, and unlike $\mathcal{H}_{DC}$, as a basis for going beyond such approximations? The purpose of this paper is to discuss these questions.

The difficulty associated with $\mathcal{H}_{DC}$ is related to the fact that $\mathcal{H}_{DC}$ corresponds to the use of Dirac's "one-electron theory." When there is only one electron in an external field, this theory is more or less equivalent to Dirac's "hole theory," i.e., to quantum electrodynamics (QED). However, when there are two or more electrons present and these electrons are allowed to interact, Dirac's one-electron theory

breaks down and one must use QED to get sensible results. If QED is used, one never gets into the trouble described above. As an example, use of an external-field Bethe-Salpeter equation,[3] derived from QED, leads to a Hamiltonian $\mathcal{H}_+$ defined by

$$\mathcal{H}_+ = \sum_{i=1}^{N} \mathcal{H}_{D;\mathrm{ext}}(i) + \mathcal{L}_+ V_{ee} \mathcal{L}_+ . \tag{1.5}$$

Here $\mathcal{L}_+$ is the projection operator onto the space $\mathcal{S}_+$ spanned by the products of the positive-energy eigenstates $u_n(i)$ of the $\mathcal{H}_{D;\mathrm{ext}}(i)$:

$$\mathcal{L}_+ = \mathcal{L}_+(1) \cdots \mathcal{L}_+(N) \tag{1.6}$$

with

$$\mathcal{L}_+(i) = \sum_n |u_n(i)\rangle\langle u_n(i)| . \tag{1.7}$$

The Hamiltonian $\mathcal{H}_+$ is an example of a relativistic many-electron Hamiltonian which does not have the difficulties associated with $\mathcal{H}_{\mathrm{DC}}$. In particular, when restricted to the subspace $\mathcal{S}_+$, the operator $\mathcal{H}_+$ can be expected to have a partially discrete spectrum and associated normalizable eigenfunctions $\psi = \psi(1,2,\ldots,N)$, which satisfy

$$\mathcal{H}_+ \psi = E\psi \tag{1.8a}$$

and

$$\mathcal{L}_+(i)\psi = \psi \quad (i = 1,2,\ldots,N) , \tag{1.8b}$$

and correspond to bound states. This is because, with $A^0_{\mathrm{ext}} = Ze/r$, there is a discrete spectrum if V_{ee} is set equal to zero, and when V_{ee} is switched on the operator $\mathcal{L}_+ V_{ee} \mathcal{L}_+$, unlike V_{ee}, does not take one out of $\mathcal{S}_+$ when acting on a function in $\mathcal{S}_+$: The projection operator $\mathcal{L}_+$ to the left of V_{ee} makes all the difference. The factor $\mathcal{L}_+$ to the right of V_{ee} could be omitted because $\mathcal{L}_+ \psi = \psi$, but it is convenient to include it because it makes the Hermiticity of $\mathcal{H}_+$ manifest.

As described in Sec. II, the operator $\mathcal{H}_+$ defined by (1.5) may be obtained more simply, without invoking the four-dimensional machinery associated with the Bethe-Salpeter equation, by expanding the quantized Dirac Field $\psi_D(\vec{x})$ in terms of the eigenfunctions of $\mathcal{H}_{D;\mathrm{ext}}$. The creation and annihilation operators defined by this expansion can in turn be used to define a "no-pair part" $H^{\mathrm{np}}_{\mathrm{mat}}$ and a "pair-part" $H^{\mathrm{pair}}_{\mathrm{mat}}$ of the matter-field Hamiltonian H_{mat}, written in Coulomb gauge, with $H^{\mathrm{np}}_{\mathrm{mat}}$ conserving suitably defined electron and positron number operators. The operator $\mathcal{H}_+$ is then just the configuration-space equivalent of the restriction of $H^{\mathrm{np}}_{\mathrm{mat}}$ to the N-electron sector of Fock space.

A Hamiltonian h_+ similar to $\mathcal{H}_+$, which shares many of the good features of $\mathcal{H}_+$ and is somewhat easier to handle in practice, is obtained when one expands $\psi_D(\vec{x})$ in the plane-wave eigenfunctions of $\vec{\alpha}\cdot\vec{p} + \beta m$; h_+ is defined by[4,5]

$$h_+ = \sum_{i=1}^{N} \mathcal{H}_D(\vec{p}_i) + \Lambda_+ (V_{\mathrm{ext}} + V_{ee}) \Lambda_+ , \tag{1.9}$$

where $\mathcal{H}_D(\vec{p}_i)$ is the free Dirac Hamiltonian and V_{ext} is the total interaction with the external field,

$$\begin{aligned} \mathcal{H}_D(\vec{p}_i) &= \vec{\alpha}_i \cdot \vec{p}_i + \beta_i m , \\ V_{\mathrm{ext}} &= -e \sum_{i=1}^{N} [A^0_{\mathrm{ext}}(\vec{r}_i) - \vec{\alpha}_i \cdot \vec{A}_{\mathrm{ext}}(\vec{r}_i)] . \end{aligned} \tag{1.10}$$

Here Λ_+ is the projection operator onto the space S_+ spanned by the products of the positive-energy plane-wave eigenstates $u_\sigma(\vec{k})\exp(i\vec{k}\cdot\vec{r}_i)$ of the $\mathcal{H}_D(\vec{p}_i)$. This time we may write more concretely

$$\Lambda_+ = \Lambda_+(1) \cdots \Lambda_+(N) , \tag{1.11}$$

where, with $E(\vec{p}) \equiv (\vec{p}^2 + m^2)^{1/2}$, the operator $\Lambda_+(i)$ defined by

$$\Lambda_+(i) = [E(\vec{p}_i) + \mathcal{H}_D(\vec{p}_i)]/2E(\vec{p}_i) , \tag{1.12}$$

is the familiar Casimir positive-energy projection operator associated with $\mathcal{H}_D(\vec{p}_i)$. In analogy with $\mathcal{H}_+$, the operator h_+ can be expected to have normalizable eigenfunctions $\phi = \phi(1,2,\ldots,N)$ satisfying

$$h_+ \phi = E\phi \tag{1.13a}$$

and

$$\Lambda_+(i)\phi = \phi \quad (i = 1,2,\ldots,N) . \tag{1.13b}$$

As explained in Sec. IIC, the most important effects of the exchange of virtual transverse photons between the atomic electrons can be taken into account by including the Breit operator

$$B_{ij} = (-e^2/2r_{ij})(\vec{\alpha}_i \cdot \vec{\alpha}_j + \vec{\alpha}_i \cdot \hat{r}_{ij} \vec{\alpha}_j \cdot \hat{r}_{ij}) \tag{1.14}$$

in the Hamiltonians $\mathcal{H}_+$ or h_+, i.e., by using the operators

$$\mathcal{H}'_+ = \sum_i \mathcal{H}_{D;\mathrm{ext}}(i) + \mathcal{L}_+ (V_{ee} + B_{ee}) \mathcal{L}_+ \tag{1.15}$$

or

$$h'_+ = \sum_i \mathcal{H}_D(\vec{p}_i) + \Lambda_+ (V_{\mathrm{ext}} + V_{ee} + B_{ee}) \Lambda_+ , \tag{1.16}$$

where

$$B_{ee} = \sum_{i<j} B_{ij} . \tag{1.17}$$

Thus, instead of looking for approximate solutions to Eqs. (1.8) or (1.13), one may equally well study the equations

$$\mathcal{H}'_+ \psi' = E\psi' \tag{1.18a}$$

with the constraint

$$\mathcal{L}_+(i)\phi' = \phi' \quad (i = 1, 2, \ldots, N) \tag{1.18b}$$

or

$$h'_+\phi' = E\phi' , \tag{1.19a}$$

with the constraint

$$\Lambda_+(i)\phi' = \phi' \quad (i = 1, 2, \ldots, N) . \tag{1.19b}$$

The ancient caveat against using the Breit operator in higher orders than the first need not be heeded here: The presence of the projection operators $\mathcal{L}_+$ or Λ_+ guarantees that no spuriously large terms are generated by the use of $\mathcal{L}_+ B_{ee} \mathcal{L}_+$ or $\Lambda_+ B_{ee} \Lambda_+$ in higher orders. Equations (1.18) and (1.19) have the advantage over (1.8) and (1.13) of containing, in a v/c expansion, all the familiar operators associated with fine structure.

For the case $N = 2$, the operator $\mathcal{H}_+$ was apparently first used long ago in a calculation of the $\alpha^3\mathcal{R}$ corrections to the fine structure of helium, where it emerged in a natural way from a study of the Bethe-Salpeter equation for two electrons in an external field.[3] It has also been used more recently in an extension of these calculations to terms of order $\alpha^4\mathcal{R}$.[6] The operator h'_+ has been found convenient in a study of relativistic M1 transitions in He and He-like ions[4,5] and its analog for the two-body problem, i.e., with the external potential switched off, has been applied to radiative M1 decays of the psions, within the framework of the charmonium model.[7,5] However, the possible utility of such operators in providing a starting point for a systematic approach to the calculation of relativistic effects in many-electron atoms appears not to have been stressed sufficiently up to now.[8] Renewed interest in this question has arisen from a study of the theoretical foundations of the calculation of parity-violating effects in heavy atoms.[9]

Mention should be made of the work of M. H. Mittleman,[10] who has also discussed configuration-space equations for many-electron atoms obtained from field theory which involve positive-energy projection operators. However, these equations are obtained from a variational ansatz made directly in Fock space, so that the projection operators themselves depend on the solution to the variational problem. The equations are therefore highly nonlinear and progress along this line appears to be difficult.

I now outline the rest of this paper. In Sec. II the "$\mathcal{H}$-type" and "h-type" relativistic wave equations are derived from quantum electrodynamics (QED). These derivations exhibit the connection between the configuration-space wave functions and the state vector lying in the sector of Fock space with charge $Q = -eN$; more importantly, it shows how one may go further and take into account not only transverse photons as in (1.15) or (1.16) but also virtual electron-positron pairs. Although a part of this material can be found elsewhere,[5,10] I include it in order to make the discussion self-contained. In Sec. III, Hartree-Fock approximations to the various wave functions are defined, and the associated relativistic HF equations are derived. The results are then used to clarify the meaning of the DHF wave function χ. In Sec. IV, the reduction of both the $\mathcal{H}$-type and h-type equations to a relativistic Schrödinger-Pauli (SP) form is carried out; this can be done in closed form without nonrelativistic approximations or the use of inverse operators which depend on the energy. The HF equations arising from the relativistic SP-type Hamiltonians are discussed in Appendix A and the nonrelativistic limit is studied in Appendix B. A summary and concluding discussion is given in Sec. V.

II. NO-PAIR HAMILTONIANS FROM QED

A. No-pair Hamiltonians in Fock space

In Coulomb gauge, the Hamiltonian H of QED is given by

$$H = H_{\rm em} + H_D + H_{\rm ext} + H_C + H_T , \tag{2.1}$$

where $H_{\rm em}$ is the energy operator for the transverse radiation field $\vec{A}_T(\vec{x})$ and H_D is the operator for the Dirac matter field $\psi_D(\vec{x})$ in the Schrödinger picture. The operators $H_{\rm ext}$, H_C, and H_T, represent the interaction of ψ_D with an external static potential $A^\mu_{\rm ext}(\vec{x})$, the Coulomb energy associated with the charge density $j^0(\vec{x})$, and the interaction of the current density $\vec{j}(\vec{x})$ with $\vec{A}_T(\vec{x})$, respectively.[11] The operators in (2.1) which do not involve $\vec{A}_T(\vec{x})$ have the form

$$H_D = \int \psi_D^\dagger(\vec{x})(\vec{\alpha}\cdot\vec{p} + \beta m)\psi_D(\vec{x})\, d\vec{x} , \tag{2.2}$$

$$H_{\rm ext} = \int j_\mu(\vec{x}) A^\mu_{\rm ext}(\vec{x})\, d\vec{x} , \tag{2.3}$$

and

$$H_C = \tfrac{1}{2}\iint \frac{j^0(\vec{x})\, j^0(\vec{x}')}{|\vec{x} - \vec{x}'|} , \tag{2.4}$$

where $j^\mu(x) = -e{:}\psi_D(\vec{x})\gamma^\mu\psi_D(\vec{x}){:}$ is the electromagnetic current. Let us suppose that H_T can be treated by perturbation theory. We are then still faced with the problem of diagonalizing the Hamiltonian $H_{\rm mat}$ describing the matter field in interaction with the external potential and with itself,

$$H_{\rm mat} = H_D + H_{\rm ext} + H_C . \tag{2.5}$$

The major difficulty with the operator $H_{\rm mat}$ is that

it does not conserve the number of electrons and positrons separately. However, it is possible to split off from $H_{\rm mat}$ a "pair part" which involves the creation or destruction of virtual electron-positron pairs and which can in many cases be treated as a perturbation, along with H_T. The remaining part of $H_{\rm mat}$, the "no-pair part," then commutes with the electron and positron number operators so that the eigenvalue problem it poses is equivalent to the problem of solving a relativistic many-particle wave equation.

The definition of the pair part or, equivalently, the no-pair part of $H_{\rm mat}$ is not unique. There are two natural alternatives, the choice of which depends on whether or not the interaction of the Dirac matter field with the external field is included in the zero-order Hamiltonian.

Let $\{u_n(\vec{x})\}$ and $\{v_m(\vec{x})\}$ denote complete orthonormal sets of positive- and negative-energy solutions of the external-field one-electron Dirac Hamiltonian

$$\mathcal{H}_{D;\rm ext}(\vec{x}) \equiv \vec{\alpha}\cdot[\vec{p}+e\vec{A}_{\rm ext}(\vec{x})] + \beta m - eA^0_{\rm ext}(\vec{x}) . \tag{2.6}$$

Then we may, on the one hand, define "external-field" electron and positron destruction operators $A(n)$ and $B(m)$ by writing, as in the Furry bound-state interaction picture,

$$\psi_D(\vec{x}) = \sum_n A(n)u_n(\vec{x}) + \sum_m B^\dagger(m)v_m(\vec{x}) . \tag{2.7}$$

On the other hand, even if $A^\mu_{\rm ext}\neq 0$, we may define "free" electron and positron destruction operators $a_\sigma(\vec{k})$ and $b_\sigma(\vec{k})$, by expanding $\psi_D(\vec{x})$ in terms of the plane-wave eigenfunctions $u_\sigma(\vec{k})\exp(i\vec{k}\cdot\vec{x})$ and $v_\sigma(\vec{k})\exp(i\vec{k}\cdot\vec{x})$ of the free Dirac Hamiltonian

$$\mathcal{H}_D(\vec{x}) = \vec{\alpha}\cdot\vec{p}+\beta m . \tag{2.8}$$

Thus an alternative to (2.7) is the more familiar expression

$$\psi_D(\vec{x}) = \sum_{\vec{k},\sigma}[a_\sigma(\vec{k})u_\sigma(\vec{k})e^{i\vec{k}\cdot\vec{x}} + b^\dagger_\sigma(\vec{k})v_{-\sigma}(-\vec{k})e^{-i\vec{k}\cdot\vec{x}}] . \tag{2.9}$$

The two choices (2.7) and (2.9) correspond to different definitions of creation and annihilation operators and hence lead to different definitions of the no-pair and pair parts of $H_{\rm mat}$. With the choice (2.7) we are led to define the no-pair part of $H_{\rm mat}$ by

$$H^{\rm np}_{\rm mat} = H_{D;\rm ext} + H^{\rm np}_C , \tag{2.10}$$

where

$$H_{D;\rm ext} = \int \psi^\dagger_D(\vec{x})\mathcal{H}_{D;\rm ext}(\vec{x})\psi_D(\vec{x})\,d\vec{x} = H_D + H_{\rm ext} \tag{2.11}$$

and $H^{\rm np}_C$ is the part of H_C which remains when (2.7) is substitued into (2.4) and only terms like $(A^\dagger A)(A^\dagger A)$ or $(A^\dagger A)(B^\dagger B)$ are kept, but terms like $(A^\dagger B^\dagger)(A^\dagger A)$ or $(A^\dagger B^\dagger)(AB)$, which involve creation or destruction of virtual pairs, are dropped.[12] Then

$$H_{\rm mat} = H^{\rm np}_{\rm mat} + H^{\rm pair}_{\rm mat} , \tag{2.12}$$

where

$$H^{\rm pair}_{\rm mat} = H_C - H^{\rm np}_C . \tag{2.13}$$

Note that with the choice (2.7), $H_{D;\rm ext}$ does not have a pair part because of the orthogonality of the eigenfunctions of $\mathcal{H}_{D;\rm ext}(\vec{x})$.

With the choice (2.9), we define the no-pair part of $H_{\rm mat}$ by

$$\tilde{H}^{\rm np}_{\rm mat} = H_D + \tilde{H}^{\rm np}_{\rm ext} + \tilde{H}^{\rm np}_C , \tag{2.14}$$

where H_D is defined by (2.2) and $\tilde{H}^{\rm np}_{\rm ext}$ is the no-pair part of $H_{\rm ext}$, obtained by substituting the expansion (2.9) into (2.3) and keeping only the scattering-type terms $a^\dagger a$ and $b^\dagger b$. The operator $\tilde{H}^{\rm np}_C$ is similarly obtained by keeping only scattering terms like $(a^\dagger a)(a^\dagger a)$, etc.; it is *not* the same as $H^{\rm np}_C$ because different creation and destruction operators are involved. The decomposition of $H_{\rm mat}$, corresponding to the definition (2.14) is then

$$H_{\rm mat} = \tilde{H}^{\rm np}_{\rm mat} + \tilde{H}^{\rm pair}_{\rm mat} , \tag{2.15}$$

where

$$\tilde{H}^{\rm pair}_{\rm mat} = \tilde{H}^{\rm pair}_{\rm ext} + \tilde{H}^{\rm pair}_C \tag{2.16}$$

with

$$\tilde{H}^{\rm pair}_{\rm ext} = \tilde{H}_{\rm ext} - \tilde{H}^{\rm np}_{\rm ext}, \quad \tilde{H}^{\rm pair}_C = H_C - \tilde{H}^{\rm np}_C . \tag{2.17}$$

B. No-pair Hamiltonians in configuration space

The operator $H^{\rm np}_{\rm mat}$ commutes with the electron and positron number operators $\mathfrak{N}_e$ and $\mathfrak{N}_p$ defined by

$$\mathfrak{N}_e = \sum_n A^\dagger(n)A(n), \quad \mathfrak{N}_p = \sum_n B^\dagger(n)B(n) . \tag{2.18}$$

We may therefore look for the state vectors Ψ which satisfy

$$\mathfrak{N}_e\Psi = N\Psi , \quad \mathfrak{N}_p\Psi = 0 \tag{2.19a}$$

and

$$H^{\rm np}_{\rm mat}\Psi = E\Psi . \tag{2.19b}$$

This eigenvalue problem is equivalent to one in configuration space for a suitably defined multi-Dirac-spinor wave function $\psi = \psi(\vec{r}_1,\ldots,\vec{r}_N)$ associated with Ψ. We define ψ by

$$\psi = \frac{1}{\sqrt{N!}}\sum_{n_1,\ldots,n_N} u_{n_1}(\vec{r}_1)\cdots u_{n_N}(\vec{r}_N) \times\langle A^\dagger(n_1)\cdots A^\dagger(n_N)\Psi_0|\Psi\rangle , \tag{2.20}$$

where Ψ_0 is the vacuum state. It follows that ψ belongs to the space $\mathcal{S}_+$ spanned by the products of the positive-energy solutions $u_n(\vec{x}_i)$ of $\mathcal{H}_D^{\text{ext}}(\vec{x}_i)$, so that

$$\mathcal{L}_+(i)\psi = \psi \quad (i = 1, \ldots, N), \tag{2.21a}$$

where $\mathcal{L}_+(i)$ is the external-field positive-energy projection operator defined by (1.7). The configuration-space equivalent of (2.19b) is readily found to be

$$\mathcal{H}_+\psi = E\psi, \tag{2.21b}$$

where $\mathcal{H}_+$ is given by (1.5). Thus, Eq. (2.21b) coincides with Eq. (1.8a) of Sec. I, and the field-theoretic origin of this equation is explained.

Equation (1.13) may be derived in an entirely analogous manner from the operator $\tilde{H}_{\text{mat}}^{\text{np}}$. The number operators which commute with $\tilde{H}_{\text{mat}}^{\text{np}}$ are

$$\tilde{\mathfrak{N}}_e = \sum_{\vec{k},\sigma} a_\sigma^\dagger(\vec{k}) a_\sigma(\vec{k}), \quad \tilde{\mathfrak{N}}_p = \sum_{\vec{k},\sigma} b_\sigma^\dagger(\vec{k}) b_\sigma(\vec{k}) \tag{2.22}$$

and the analogs of (2.19a) and (2.19b) are

$$\tilde{\mathfrak{N}}_e \Phi = N\Phi, \quad \tilde{\mathfrak{N}}_p \Phi = 0 \tag{2.23a}$$

and

$$\tilde{H}_{\text{mat}} \Phi = E\Phi. \tag{2.23b}$$

With $\phi = \phi(\vec{r}_1, \ldots, \vec{r}_N)$ defined by

$$\phi = \frac{1}{\sqrt{N!}} \sum_{(\vec{k}_i, \sigma_i)} u_{\sigma_1}(\vec{k}_1) \cdots u_{\sigma_N}(\vec{k}_N) \times \langle a_{\sigma_1}^\dagger(\vec{k}_1) \cdots a_{\sigma_N}^\dagger(\vec{k}_N) \Phi_0 | \Phi \rangle, \tag{2.24}$$

where Φ_0 is the vacuum state, we get as the analog of (2.21),

$$\Lambda_+(i)\psi = \psi \quad (i = 1, \ldots, N), \tag{2.25a}$$

where $\Lambda_+(i)$ is the Casimir projection operator defined by (1.12), and

$$h_+ \phi = E\phi. \tag{2.25b}$$

Here h_+ is defined by (1.9) so that Eq. (2.25b) coincides with (1.13b). Thus the field-theoretic origin of this equation is also made manifest.

In Sec. III we study HF approximations to the solutions ψ and ϕ of Eqs. (2.21) and (2.25), respectively. However, first we consider how effects not included in $\mathcal{H}_+$ or h_+ can in principle be calculated, by returning to the Fock-space Hamiltonians H and $H_{\text{mat}}^{\text{np}}$.

C. Photons and virtual electron-positron pairs

With the definition (2.10) for the Hamiltonian $H_{\text{mat}}^{\text{np}}$, the total Hamiltonian may be written as

$$H = H_0 + H', \tag{2.26a}$$

where

$$H_0 = H_{\text{em}} + H_{\text{mat}}^{\text{np}} \tag{2.26b}$$

and

$$H' = H_T + H_C^{\text{pair}}. \tag{2.26c}$$

The residual interaction H' can normally be treated by perturbation theory and the problem of calculating level shifts and transition amplitudes can be formulated in a straightforward way.

As an example, the amplitude for a one-photon transition $\Psi_a \to \Psi_b + \gamma$, where Ψ_a and Ψ_b denote N-electron eigenstates of $H_{\text{mat}}^{\text{np}}$, is given by

$$\mathfrak{M}_{ba} = \langle \Psi_b; \vec{k}, \vec{\epsilon} \, | H' + H'(E_a - H_0 + i\epsilon)^{-1} H' + \cdots | \Psi_a \rangle. \tag{2.27}$$

The leading-order term in (2.27), proportional to e, is

$$\mathfrak{M}_{ba}^{(1)} = \frac{e}{\sqrt{2\omega}} \left\langle \psi_b \middle| \sum_i \vec{\alpha}_i \cdot \vec{\epsilon}\, e^{-i\vec{k}\cdot\vec{r}_i} \middle| \psi_b \right\rangle. \tag{2.28}$$

Although this is certainly a familiar looking formula, it differs from the usual one in that the wave functions ψ_a and ψ_b are well defined as solutions of a *bona fide* eigenvalue problem (1.8). Of course in practice approximations will have to be made for ψ_a and ψ_b, but at least one knows what quantity it is that is being approximated.

The level shift in the state Ψ_a arising from H' is given by

$$\Delta E_a = \langle \Psi_a | H' + H'(E_a - H_0 + i\epsilon)^{-1} H' + \cdots | \Psi_a \rangle. \tag{2.29}$$

The leading term in (2.29), proportional to e^2, is

$$\Delta E_a^{(2)} = \langle \Psi_a | H_T (E_a - H_0 + i\epsilon)^{-1} H_T | \Psi_a \rangle. \tag{2.30}$$

One can write

$$H_T = H_T^{\text{np}} + H_T^{\text{pair}}, \tag{2.31}$$

where the no-pair part H_T^{np} of H_T involves only $A^\dagger A$ or $B^\dagger B$ type of terms as far as matter field creation and annihilation operators are concerned. H_T^{pair} contributes only to what are effectively one-electron self-energy effects as do the parts of the term coming from $H_T^{\text{np}} \cdots H_T^{\text{np}}$ in which a photon is absorbed by the same electron which emits it. These contributions are, after renormalization subtractions, small compared to the remaining part which corresponds to one-photon exchange between (different) electrons. This is given by

$$\Delta E_{1\gamma}^{(2)} = e^2 \int \frac{d\vec{k}}{(2\pi)^3} \sum_{\lambda=1}^{2} M_\lambda(\vec{k}), \tag{2.32}$$

where

$$M_\lambda(\vec{k}) = \frac{1}{2\omega} \sum_{i \neq j} \left\langle \psi_a \middle| \zeta_i^\dagger \frac{\mathcal{L}_+}{E_a - \omega - \mathcal{H}_+ + i\epsilon} \zeta_j \middle| \psi_a \right\rangle + \text{c.c.}, \tag{2.33}$$

with $\zeta_i = \vec{\alpha}_i \cdot \vec{\epsilon}_\lambda \exp(i\vec{k}\cdot\vec{r}_i)$ and $\mathcal{L}_+$ the positive-energy projection operator (1.6). If electron recoil energies are neglected, we get

$$M_\lambda(\vec{k}) \approx (-1/2\omega^2) \sum_{i\neq j} \langle \psi_a | \zeta_i^\dagger \mathcal{L}_+ \zeta_j + \zeta_j^\dagger \mathcal{L}_+ \zeta_i | \psi_a \rangle . \quad (2.34)$$

Since the factors $\mathcal{L}_+(i)$ and $\mathcal{L}_+(j)$ in $\mathcal{L}_+$ commute with ζ_j and ζ_i, respectively, and $\mathcal{L}_+(i)\psi_a = \psi_a$, the operator $\mathcal{L}_+$ in (2.34) may be replaced by unity. The integration on $\vec{k}$ can then be carried out and we get the familiar result

$$\Delta E_{1\gamma}^{(2)} \approx \Delta E_B \equiv \sum_{i<j} \langle \psi_a | B_{ij} | \psi_a \rangle , \quad (2.35)$$

where

$$B_{ij} = (-e^2/2r_{ij})(\vec{\alpha}_i \cdot \vec{\alpha}_j + \vec{\alpha}_i \cdot \hat{r}_{ij} \vec{\alpha}_j \cdot \hat{r}_{ij}) \quad (2.36)$$

is the Breit operator. However, in contrast to the usual situation one can add B_{ij} to e^2/r_{ij} in the zero-order Hamiltonians $\mathcal{H}_+$ or h_+ without generating spurious effects.[13] Thus one can equally well use the operator

$$\mathcal{H}_+' = \sum_i \mathcal{H}_{D;\text{ext}}(i) + \mathcal{L}_+ \sum_{i<j} \left(\frac{e^2}{r_{ij}} + B_{ij} \right) \mathcal{L}_+ \quad (2.37)$$

or

$$h_+' = \sum_i \mathcal{H}_D(i) + \Lambda_+ \left[\sum_i V_{\text{ext}}(\vec{r}_i) + \sum_{i<j} \left(\frac{e^2}{r_{ij}} + B_{ij} \right) \right] \Lambda_+ \quad (2.38)$$

as a starting point for approximate calculations. The leading effects of one-photon exchange will then automatically be included and some of the effects of the exchange of more than one photon will also be taken into account thereby.

To be precise, inclusion of B_{ij} in (2.37) and (1.18) is equivalent to the approximate summation of all those time-ordered Feynman-type diagrams, not involving self-energy effects or radiative corrections to virtual-photon emission, in which (i) one or more photons are exchanged between the electrons, (ii) no more than one photon is "in the air" at any time, and (iii) no electron-positron pairs occur in intermediate states. The summation is inexact because of the neglect of electron recoil energy in intermediate states.

III. HARTREE-FOCK EQUATIONS

The derivation of relativistic HF equations based on $\mathcal{H}_+$ or h_+ is straightforward. The only difference from the usual procedure is the need to take into account the positive-energy constraint (1.8b) or (1.13b).

A. HF equations from H_+

For simplicity we consider only an unrestricted, single-configuration HF approximation. Let $\{\psi_i(1)\}$ denote an orthonormal set of N external-field positive-energy Dirac orbitals. Thus the ψ_i satisfy

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \quad (3.1)$$

and

$$\mathcal{L}_+(1)\psi_i(1) = \psi_i(1) , \quad (3.2)$$

where $\mathcal{L}_+(1)$ is the external-field projection operator defined by (1.7). To get an approximation ψ^{HF} to an eigenfunction ψ of $\mathcal{H}_+$ we construct the Slater determinant

$$\psi^{\text{HF}} = (1/\sqrt{N!})\,\text{Det}[\psi_1(1)\psi_2(2)\cdots\psi_N(N)] \quad (3.3)$$

and require that $\langle \psi^{\text{HF}} | \mathcal{H}_+ | \psi^{\text{HF}} \rangle$ is stationary under variations of the ψ_i, subject to the constraints (3.1) and (3.2). Because $\mathcal{L}_+^2(1) = \mathcal{L}_+(1)$, the condition (3.2) is equivalent to

$$\langle \psi_i | \mathcal{L}_+(1) - 1 | \psi_i \rangle = 0 . \quad (3.4)$$

Thus an appropriate variational functional is

$$\mathcal{F}[\psi^{\text{HF}}] = \langle \psi^{\text{HF}} | \mathcal{H}_+ | \psi^{\text{HF}} \rangle - \sum_{ij} \lambda_{ij} \langle \psi_i | \psi_j \rangle - \sum_i \nu_i \langle \psi_i | \mathcal{L}_+(1) - 1 | \psi_i \rangle ,$$

where the λ_{ij} and ν_i are Lagrangian multipliers. The requirement that $\delta\mathcal{F} = 0$ for arbitrary variations $\delta\psi_i$ then leads to equations which, after use is made of the constraint (3.2), may be written in the form

$$\mathcal{H}_{D;\text{ext}}(1)\psi_i(1) + \mathcal{L}_+(1)\mathfrak{U}_i(1)\mathcal{L}_+(1)\psi_i(1) - \sum_{j\neq i} \mathcal{L}_+(1)\mathfrak{U}_{ji}(1)\mathcal{L}_+(1)\psi_j(1) = \sum_j \lambda_{ij}\psi_j(1) , \quad (3.5)$$

where

$$\mathfrak{U}_{ij}(1) = \langle \psi_i(2) | e^2/r_{12} | \psi_j(2) \rangle \quad (3.6a)$$

and

$$\mathfrak{U}_i(1) = \sum_{j\neq i} \mathfrak{U}_{jj}(1) . \quad (3.6b)$$

Equation (3.5) differs from the corresponding DHF equation only in the presence of the projection operator $\mathcal{L}_+(1)$ standing to the left and right of all terms which arise from the electron-electron Coulomb interaction. As for the DHF equations, the λ_{ij} must be chosen so as to satisfy the constraint (3.1). Positive-energy analogs of, e.g., the restricted DHF equations can be derived in an entirely similar manner: They differ from the latter only in the $\mathcal{L}_+(1)$ factors. Of course if

one tries to solve such equations numerically, the constraint (3.2) must be taken into account. We return to this point later.

B. HF equations from h_+

In analogy with Eqs. (3.1) and (3.2) we consider an orthonormal set $\{\phi_i(1)\}$ of free positive-energy Dirac orbitals. Thus the ϕ_i satisfy

$$\langle\phi_i|\phi_j\rangle=\delta_{ij} \tag{3.7}$$

and

$$\Lambda_+(1)\phi_i(1)=\phi_i(1)\,, \tag{3.8}$$

where $\Lambda_+(1)$ is the free positive-energy projection operator defined by (1.12). A Hartree-Fock approximation ϕ^{HF} to an eigenfunction ϕ of h_+ is now defined by

$$\phi^{HF}=(1/\sqrt{N}!)\,\mathrm{Det}[\phi_1(1)\phi_2(2)\cdots\phi_N(N)]\,. \tag{3.9}$$

On applying the variational principle to $\langle\phi^{HF}|h_+|\phi^{HF}\rangle$ one gets, in obvious analogy with (3.5), the result

$$\mathcal{K}_D(1)\phi_i(1)+\Lambda_+(1)V_i(1)\Lambda_+(1)\phi_i(1)$$
$$-\sum_{j\neq i}\Lambda_+(1)U_{ji}(1)\Lambda_+(1)\phi_j(1)=\sum_j\lambda_{ij}\phi_j\,, \tag{3.10}$$

where

$$U_{ij}(1)=\langle\phi_i(2)|e^2/r_{12}|\phi_j(2)\rangle\,, \tag{3.11a}$$

and

$$V_i(1)=-eA^0_{\mathrm{ext}}(1)+e\vec{\alpha}_1\cdot\vec{A}_{\mathrm{ext}}(1)$$
$$+\sum_{j\neq i}U_{jj}(1)\,. \tag{3.11b}$$

Again, (3.10) differs from the corresponding DHF equation only in the projection-operator factors $\Lambda_+(1)$.

C. Interpretation of the DHF wave function χ

For equations like (3.5) or (3.10), normalizable solutions can exist even if the projection operators $\mathcal{L}_+(1)$ or $\Lambda_+(1)$ are omitted. Moreover, in the nonrelativistic limit, $\alpha Z\ll 1$, the operators $\mathcal{L}_+(1)$ and $\Lambda_+(1)$ may be replaced by unity in Eqs. (3.5) and (3.10). It follows that, at least if αZ is not too large, the orbitals $\chi_i(\vec{r})$ associated with the (unrestricted) HF equations arising from $\mathcal{K}_{DC}$ can be regarded as approximations to the orbitals ψ_i or ϕ_i defined by the solutions of Eq. (3.5) or (3.10), respectively, as discussed in more detail in Sec. III E below. Hence the DHF wave function χ can be viewed as an approximation to ψ^{HF} or ϕ^{HF} and therefore to the functions ψ or ϕ, both of which have a precise theoretical definition within the framework of QED. A similar interpretation can be given to restricted, extended, or other types of DHF wave functions: For each type,[14] there is a corresponding approximation to ψ or ϕ which satisfies an analogous set of relativistic HF equations.

D. HF equations from H'_+ or h'_+

Use of the operator $\mathcal{K}'_+$ and h'_+, defined by (2.37) and (2.38), leads to HF equations fully analogous to (3.5) and (3.10). Thus, with $\psi'_i(\vec{r})$ and $\phi'_i(\vec{r})$ the orbitals associated with Slater determinants ψ'^{HF} and ϕ'^{HF} we get

$$\mathcal{K}_{D;\mathrm{ext}}(1)\psi'_i(1)+\mathcal{L}_+(1)\mathfrak{U}'_i(1)\mathcal{L}_+(1)\psi'_i(1)$$
$$-\sum_{j\neq i}\mathcal{L}_+(1)\mathfrak{U}'_{ji}(1)\mathcal{L}_+(1)\psi'_j(1)=\sum_j\lambda_{ij}\psi'_j(1) \tag{3.12a}$$

with

$$\mathfrak{U}'_{ij}(1)=\langle\psi'_i(2)|e^2/r_{12}+B_{12}|\psi'_j(2)\rangle\,,$$
$$\mathfrak{U}'_i(1)=\sum_{j\neq i}\mathfrak{U}'_{jj}(1) \tag{3.12b}$$

and

$$\mathcal{K}_D(1)\phi'_i(1)+\Lambda_+(1)V'_i(1)\Lambda_+(1)\phi'_i(1)$$
$$-\sum_{j\neq i}\Lambda_+(1)\mathfrak{U}_{ji}(1)\Lambda_+(1)\phi'_j(1)=\sum_j\lambda_{ij}\phi'_j(1) \tag{3.13a}$$

with

$$U'_{ij}(1)=\langle\phi'_i(2)|e^2/r_{12}+B_{12}|\phi'_j(2)\rangle\,,$$
$$V'_i(1)=-eA^0_{\mathrm{ext}}(1)+e\vec{\alpha}_1\cdot\vec{A}_{\mathrm{ext}}(1)+\sum_{j\neq i}U'_{jj}(1)\,. \tag{3.13b}$$

In analogy with (3.2) and (3.8) the orbitals must satisfy the constraints

$$\mathcal{L}_+(1)\psi'_i(1)=\psi'_i(1) \tag{3.14}$$

and

$$\Lambda_+(1)\phi'_i(1)=\phi'_i(1)\,. \tag{3.15}$$

These equations are further discussed in Appendix A.

E. Relation between the orbitals

The relation between the orbitals χ_i associated with the DHF equations and the orbitals ϕ_i and ψ_i merits further discussion. It is convenient to first consider the connection between the upper components f_i^U and lower components f_i^L in each case. Because χ_i is neither an eigenfunction of Λ_+ nor of $\mathcal{L}_+$ one must use the DHF equation $(\vec{\alpha}\cdot\vec{p}+\beta m+V_i^{\mathrm{eff}})\chi_i=\epsilon_i\chi_i$ to obtain the connection between χ_i^L and χ_i^U, whereas for ϕ_i and ψ_i the constraint equations (3.8) and (3.2) can be used directly, as described in more detail in Sec. IV. The result can be written in the form

$$f_i^L = \frac{\vec{\sigma}\cdot\vec{p}}{2m} f_i^U + \delta f_i^L ,$$

where δf_i^L is a correction to the leading term $\vec{\sigma}\cdot\vec{p} f_i^U/2m$. Computation shows that (i) relative to the leading term, $\delta\chi_i^L$ is of order $\langle V_i^{\rm eff}/m\rangle \sim (\alpha Z_i^{\rm eff})^2$, where $Z_i^{\rm eff}$ is an effective charge, of order Z for the innermost orbits and of order unity for the outermost orbits; (ii) $\delta\phi_i^L$ is of order $\langle \vec{p}^2/m^2\rangle$ relative to the leading term, i.e., also of relative order $(\alpha Z_{\rm eff})^2$; (iii) $\delta\psi_i^L$ involves corrections not only of order $\langle \vec{p}^2/m^2\rangle$ but also of order $\langle V_{\rm ext}/m\rangle$ and hence is of order $ZZ_i^{\rm eff}\alpha^2$ relative to the leading term. Thus in all cases δf_i^L is quite small except for large Z ($\gtrsim$45 say) and the innermost orbits. The character of the large components f_i^U can now be ascertained by eliminating $f_i^L \approx \vec{\sigma}\cdot\vec{p} f_i^U/2m$ from the HF equations and comparing the reduced equations with each other. These equations turn out to differ only in interaction terms of relative order $(\alpha Z)^6 m$ or smaller, so that one concludes, e.g., that $\chi_i^U = (1+a_i)\psi_i^U$, where a_i is of order $(\alpha Z)^4$ or smaller. This in turn implies that $\chi_i^L = (1+b_i)\psi_i^L$, where b_i is of order $(\alpha Z)^2$ or smaller.

This analysis shows also how a solution $\{\chi_i\}$ of the DHF equations can be used to obtain a good starting point $\{\tilde{\psi}_i\}$ or $\{\tilde{\phi}_i\}$ for obtaining a self-consistent solution of (3.5) or (3.10). For example, one may take $\tilde{\phi}_i^U = \chi_i^U$ and then define $\tilde{\phi}_i^L$ so that $\Lambda_+\tilde{\phi}_i = \tilde{\phi}_i^L$, viz., $\tilde{\phi}_i = (E_p+m)^{-1}\vec{\sigma}\cdot\vec{p}\chi_i^U$. Similarly, one can take $\tilde{\psi}_i^U = \chi_i^U$ and define $\tilde{\psi}_i^L$ so that $\mathcal{L}_+\tilde{\psi}_i = \tilde{\psi}_i$. The use of these "improved" four-component orbitals presents an alternative to the procedure considered in Sec. IV in which a reduction to upper components is carried out before the HF approximation is made.

IV. REDUCTION TO PAULI FORM

Both the h-type and the more complicated $\mathcal{H}$-type relativistic wave equations derived in Sec. II can be reduced to equations of the Schrödinger-Pauli (SP) type. The reduction can be carried out in closed form, without any change in the linear character of the eigenvalue problem. With regard to the $\mathcal{H}$-type equations this possibility may appear to be in sharp contrast to the situation which arises for the ordinary one-electron Dirac equation,

$$(\vec{\alpha}\cdot\vec{\Pi} + \beta m - eA_{\rm ext}^0)u = Eu , \tag{4.1}$$

where $\vec{\Pi} \equiv \vec{p} + e\vec{A}_{\rm ext}$. With $u^{(\pm)} = (1\pm\beta)u/2$, the usual reduction of (4.1) leads to

$$[\vec{\sigma}^D\cdot\vec{\Pi}(E+m+eA_{\rm ext}^0)^{-1}\vec{\sigma}^D\cdot\vec{\Pi} - eA_{\rm ext}^0]u^{(+)} = Eu^{(+)} , \tag{4.2}$$

where $\vec{\sigma}^D$ is the double of the Pauli matrix vector $\vec{\sigma}$. This equation involves an energy-dependent reduced Hamiltonian and represents a nonlinear eigenvalue problem for the large component part $u^{(+)}$ of u. However, the reduction of (4.1) can also be carried out in another way, which does lead to an energy-independent reduced Hamiltonian and a linear eigenvalue problem.[15] By following an approach similar to that used in Ref. 15, this can also be accomplished for the many-body equations (1.8) and (1.18).

A. From Dirac spinors to Pauli spinors

1. Free-field constraint

It is easy to see that any multi-Dirac spinor ϕ which satisfies the constraint

$$\Lambda_+(i)\phi = \phi \quad (i = 1,2,\ldots,N) \tag{4.3}$$

can be expressed in terms of its large component $\phi^{(+)}$, defined by

$$\phi^{(+)} \equiv \beta_1^{(+)}\cdots\beta_N^{(+)}\phi , \tag{4.4}$$

where

$$\beta_i^{(\pm)} \equiv \tfrac{1}{2}(1\pm\beta_i) . \tag{4.5}$$

One can write (4.3) in the form

$$(\vec{\alpha}_i\cdot\vec{p}_i + \beta_i m_i)\phi = E_i\phi . \tag{4.6}$$

with

$$E_i \equiv (\vec{p}_i^2 + m_i^2)^{1/2} , \tag{4.7}$$

multiply (4.6) by $\beta_i^{(-)}$, and solve for $\beta_i^{(-)}\phi$ in terms of $\beta_i^{(+)}\phi$. One then gets for $\phi = \beta_i^{(+)}\phi + \beta_i^{(-)}\phi$, the identity

$$\phi = (1+R_i)\beta_i^{(+)}\phi , \tag{4.8}$$

where

$$R_i \equiv \frac{\vec{\alpha}_i\cdot\vec{p}_i}{m+E_i} . \tag{4.9}$$

It is convenient to rewrite (4.8) in the form

$$\phi = S_i A_i^{-1}\phi , \tag{4.10}$$

where

$$S_i \equiv (1+R_i)\beta_i^{(+)}A_i . \tag{4.11}$$

One can choose the factor A_i so that S_i satisfies

$$S_i^\dagger S_i = \beta_i^{(+)} . \tag{4.12}$$

Then S_i is pseudounitary, i.e., unitary in the subspace of spinors which satisfy $\beta_i^{(+)}\phi = \phi$. The condition (4.12) is met with the choice

$$A_i = (1+R_iR_i)^{-1/2} = [(m+E_i)/2E_i)]^{1/2} . \tag{4.13}$$

Since $\beta_i^{(+)}$ commutes with A_i and the operators associated with different values of i commute with each other, repeated use of (4.10) yields the

identity

$$\phi = (S_1 A_1^{-1}) \cdots (S_N A_N^{-1})(\beta_1^{(+)} \cdots \beta_N^{(+)})\phi \,. \tag{4.14}$$

Using the definition (4.4) we may rewrite (4.14),

$$\phi = SA^{-1}\phi^{(+)} \,, \tag{4.15}$$

where

$$S \equiv S_1 \cdots S_N, \quad A \equiv A_1 \cdots A_N \,. \tag{4.16}$$

Equation (4.15) is the sought-for expression of ϕ in terms of $\phi^{(+)}$.

2. *External-field constraint*

A multi-Dirac spinor ψ which satisfies, instead of (4.3), the constraint

$$\mathcal{L}_+(i)\psi = \psi \quad (i = 1, 2, \ldots, N) \,, \tag{4.17}$$

may also be expressed in terms of its large components, at least in a formal sense. All one needs is an analog $\mathcal{E}_i$ of the operator E_i. A suitable $\mathcal{E}_i$ is the "absolute value" of $\mathcal{H}_{D;\text{ext}}(i)$, defined via

$$\mathcal{E}(i) = \sum_n \epsilon_n |u_n(i)\rangle \langle u_n(i)| \,. \tag{4.18}$$

Here the summation is over the positive-energy eigenstates $u_n(i)$ of $\mathcal{H}_{D;\text{ext}}(i)$:

$$\mathcal{H}_{D;\text{ext}}(i) u_n(i) = \epsilon_n(i) u_n(i) \tag{4.19a}$$

with $\epsilon_n > 0$ and $\mathcal{H}_{D;\text{ext}}(i)$ of the form

$$\mathcal{H}_{D;\text{ext}}(i) = \vec{\alpha}_i \cdot \vec{p}_i + \beta_i m + V(i) \,. \tag{4.19b}$$

Although $V(i) = -eA^0_{\text{ext}}(\vec{r}_i) + e\vec{\alpha}_i \cdot \vec{A}_{\text{ext}}(\vec{r}_i)$ for the case at hand, the following development can be carried out for any $V(i)$.

With the help of the operator $\mathcal{E}(i)$ the external-field projection operator $\mathcal{L}_+(i)$ may be written in a form analogous to (1.12) for $\Lambda_+(i)$,

$$\mathcal{L}_+(i) = \frac{\mathcal{E}(i) + \mathcal{H}_{D;\text{ext}}(i)}{2\mathcal{E}(i)} \,. \tag{4.20}$$

The condition (4.17) may then be written in the form

$$\mathcal{H}_{D;\text{ext}}(i)\psi = \mathcal{E}(i)\psi \,. \tag{4.21}$$

With $\rho_i \equiv \gamma_5(i)$, we can use a basis for the vector space of 4×4 matrices the four matrices $\underline{1}_i$, β_i, ρ_i, and $\beta_i\rho_i$ together with the twelve more obtained by multiplying these four by $\vec{\sigma}_i^p$. Then $\mathcal{E}(i)$ may be written in the form

$$\mathcal{E}(i) = a_i \underline{1}_i + b_i\beta_i + c_i\rho_i + d_i\beta_i\rho_i \,, \tag{4.22}$$

where the coefficients $a_i, \ldots, d_i$ *commute* with both β_i and ρ_i and have the form typified by

$$a_i = a_i^{(0)} + \vec{\sigma}_i^p \cdot \vec{a}_i^{(1)} \,. \tag{4.23}$$

Since $\vec{\alpha}_i = \vec{\sigma}_i^p \rho_i$, we obtain by multiplying (4.21) by $\beta_i^{(-)}$ and using the form (4.22) for $\mathcal{E}(i)$, together with the fact that $\beta_i^{(-)}\rho_i = \rho_i\beta_i^{(+)}$, the relation

$$\beta_i^{(-)}\psi = \mathcal{R}_i\beta_i^{(+)}\psi \,, \tag{4.24}$$

where

$$\mathcal{R}_i = [a_i - b_i + m + eA^0_{\text{ext}}(i)]^{-1} \times (\vec{\sigma}_i^p \cdot \vec{\Pi}_i - c_i + d_i)\rho_i \tag{4.25}$$

with

$$\vec{\Pi}_i \equiv \vec{p}_i + e\vec{A}_{\text{ext}}(i) \,. \tag{4.26}$$

Since $\psi = \beta_i^{(+)}\psi + \beta_i^{(-)}\psi$, we may rewrite (4.24) in the form analogous to (4.10)

$$\psi = \mathcal{S}_i \mathcal{A}_i^{-1}\psi \,, \tag{4.27}$$

where

$$\mathcal{S}_i \equiv (1 + \mathcal{R}_i)\beta_i^{(+)}\mathcal{A}_i \tag{4.28}$$

and the factor $\mathcal{A}_i$ is, so far, arbitrary. It is again possible and convenient to choose $\mathcal{A}_i$ so that

$$\mathcal{S}_i^\dagger \mathcal{S}_i = \beta_i^{(+)} \,, \tag{4.29}$$

i.e., so that $\mathcal{S}_i$ preserves scalar products in the subspace of multispinors which satisfy $\beta_i^{(+)}\psi = \psi$. Because $\mathcal{R}_i$ anticommutes with β_i, one has

$$\beta_i^{(+)}\mathcal{R}_i\beta_i^{(+)} = 0 \tag{4.30}$$

so that a suitable choice for $\mathcal{A}_i$ is readily seen to be

$$\mathcal{A}_i = (1 + \mathcal{R}_i^\dagger \mathcal{R}_i)^{-1/2} \,. \tag{4.31}$$

Since $\mathcal{A}_i$ commutes with β_i, one may use (4.27) repeatedly and write

$$\psi = \mathcal{S}\mathcal{A}^{-1}\psi^{(+)} \,, \tag{4.32}$$

where $\psi^{(+)} \equiv \beta_1^{(+)} \cdots \beta_N^{(+)}\psi$ and

$$\mathcal{S} = \mathcal{S}_1 \cdots \mathcal{S}_N, \quad \mathcal{A} = \mathcal{A}_1 \cdots \mathcal{A}_N \,. \tag{4.33}$$

Equation (4.32) expresses ψ in terms of its large-component part $\psi^{(+)}$, in exact analogy with Eq. (4.15). Note that for $A^\mu_{\text{ext}} \to 0$, $\mathcal{R}_i \to R_i$ so that $\mathcal{S} \to S$, $\mathcal{A} \to A$, and (4.32) reduces to (4.15).

B. Relativistic Schrödinger-Pauli equations

With the help of Eqs. (4.32) and (4.15), the reduction of the relativistic wave equations (1.8), (1.13), (1.18), and (1.19) to equivalent relativistic SP-type equations is readily accomplished. Because the relations (4.15) and (4.32) are independent of the electron-electron interaction, it is sufficient to consider explicitly only the "primed" equations, (1.18) and (1.19), containing the Breit operators B_{ij}. The reduced form of Eqs. (1.8) and (1.13) is obtained by dropping the terms arising from the B_{ij}. We shall consider the simpler equation (1.19) first.

1. Reduction of $h'_+\phi' = E\phi'$

Because $\Lambda_+(i)\phi' = \phi'$, we may use Eq. (4.15) to write

$$\phi' = S\phi'_P , \tag{4.34}$$

where ϕ'_P is defined by

$$\phi'_P \equiv A^{-1}\phi'^{(+)} . \tag{4.35}$$

Here $\phi'^{(+)}$ is the large-component part of ϕ'. ϕ'_P is essentially a Pauli-type wave function because the relations $[\beta_i, A] = 0$ and $\beta_i\phi'^{(+)} = \phi'^{(+)}$ assure that

$$\beta_i\phi'_P = \phi'_P . \tag{4.36}$$

Thus if the standard representation is used for the β_i, ϕ'_P has only 2^N nonvanishing components, like $\phi'^{(+)}$. The factor A^{-1} is included in the definition of ϕ'_P because the mapping (4.34) then preserves scalar products and leads to a reduced Hamiltonian which is manifestly Hermitian. Thus, from Eqs. (4.12) and (4.16) one infers that S is pseudo-unitary,

$$S^\dagger S = \beta_1^{(+)} \cdots \beta_N^{(+)} , \tag{4.37}$$

so that on use of (4.36) one gets

$$\langle \phi' | \phi' \rangle = \langle \phi'_P | \phi'_P \rangle . \tag{4.38}$$

To find the equation satisfied by ϕ'_P, we substitute (4.34) into (1.19) and multiply on the left by $S^\dagger$ to get

$$h'^{\,\mathrm{red}}_+ \phi'_P = E\phi'_P , \tag{4.39a}$$

where

$$h'^{\,\mathrm{red}}_+ \equiv S^\dagger h'_+ S . \tag{4.39b}$$

In view of Eq. (4.36), it is permissible, *after* one simplifies (4.39) by commuting all β_i operators to the right and eliminates even powers of the α's via $\vec{\alpha}\cdot\vec{a}\vec{\alpha}\cdot\vec{b} = \vec{\sigma}^D\cdot\vec{a}\vec{\sigma}^D\cdot\vec{b}$, to replace β_i by unity and $\vec{\sigma}^D$ by the 2×2 Pauli matrix vector $\vec{\sigma}$. With this understood, one can define a relativistic SP-type Hamiltonian h_P^{rel} by

$$h_P^{\mathrm{rel}} \equiv h'^{\,\mathrm{red}}_+ \big|_{\beta_i \to 1,\ \vec{\sigma}_i^D \to \vec{\sigma}_i} . \tag{4.40}$$

Now let

$$\phi_P = \phi_P(1, \ldots, N) \tag{4.41}$$

denote the multi-Pauli spinor wave function obtained by collecting together the 2^N nonvanishing components of ϕ'_P. Then (4.39) is seen to be equivalent to

$$h_P^{\mathrm{rel}}\phi_P = E\phi_P . \tag{4.42}$$

A more explicit form of h_P^{rel} is straightforward to obtain. For any operator $\mathcal{O}$ we may define an even part $\mathcal{O}_+$ which commutes with β_i and an odd part $\mathcal{O}_-$ which anticommutes with β_i by

$$\mathcal{O}_\pm = \tfrac{1}{2}(\mathcal{O} \pm \beta_i\mathcal{O}\beta_i) . \tag{4.43a}$$

Then

$$\beta_i^{\{\pm\}}\mathcal{O}_+ = \mathcal{O}_+\beta_i^{\{\pm\}}, \quad \beta_i^{\{\pm\}}\mathcal{O}_- = \mathcal{O}_-\beta_i^{\{\mp\}} , \tag{4.43b}$$

and on recalling the definition (4.11) of S_i, one gets

$$S_i^\dagger \mathcal{O}_+ S_i = A_i(\mathcal{O}_+ + R_i\mathcal{O}_+R_i)A_i\beta_i^{\{+\}} , \tag{4.43c}$$

$$S_i^\dagger \mathcal{O}_- S_i = A_i(\mathcal{O}_-R_i + R_i\mathcal{O}_-)A_i\beta_i^{\{+\}} . \tag{4.43d}$$

For example, using (4.43d) and (4.43c) one finds that

$$S_i^\dagger \vec{\alpha}_i\cdot\vec{p}_i S_i = (\vec{p}_i^{\,2}/E_i)\beta_i^{\{+\}} ,$$

$$S_i^\dagger \beta_i m S_i = (m^2/E_i)\beta_i^{\{+\}} ,$$

so that

$$S_i^\dagger \mathcal{H}_D(\vec{p}) S_i = E_i\beta_i^{\{+\}} .$$

Computation along these lines yields

$$h_P^{\mathrm{rel}} = \sum_i E_i + \sum_i V_{\mathrm{ext}}^{\mathrm{rel}}(i) + \sum_{i<j} V^{\mathrm{rel}}(i,j) , \tag{4.44}$$

where the operators $V_{\mathrm{ext}}^{\mathrm{rel}}(i)$ and $V^{\mathrm{rel}}(i,j)$ arise, respectively, from the external-field and electron-electron interaction,

$$V_{\mathrm{ext}}^{\mathrm{rel}}(i) = -eA_i[A^0_{\mathrm{ext}}(i) + \hat{R}_iA^0_{\mathrm{ext}}(i)\hat{R}_i - \hat{R}_i\vec{\sigma}_i\cdot\vec{A}_{\mathrm{ext}}(i) - \vec{\sigma}_i\cdot\vec{A}_{\mathrm{ext}}(i)\hat{R}_i]A_i \tag{4.45}$$

with

$$\hat{R}_i \equiv \frac{\vec{\sigma}_i\cdot\vec{p}_i}{m + E_i} \tag{4.46}$$

and

$$V^{\mathrm{rel}}(i,j) = A_iA_j\left(\frac{e^2}{r_{ij}} + \hat{R}_i\frac{e^2}{r_{ij}}\hat{R}_j + \hat{R}_j\frac{e^2}{r_{ij}}\hat{R}_i + \hat{R}_i\hat{R}_j\frac{e^2}{r_{ij}}\hat{R}_i\hat{R}_j\right)A_iA_j + A_iA_j(\hat{B}_{ij}\hat{R}_i\hat{R}_j + \hat{R}_i\hat{B}_{ij}\hat{R}_j + \hat{R}_j\hat{B}_{ij}\hat{R}_i + \hat{R}_i\hat{R}_j\hat{B}_{ij})A_iA_j \tag{4.47}$$

with

$$\hat{B}_{ij} \equiv (-e^2/2r_{ij})(\vec{\sigma}_i\cdot\vec{\sigma}_j + \vec{\sigma}_i\cdot\hat{r}_{ij}\vec{\sigma}_j\cdot\hat{r}_{ij}) . \tag{4.48}$$

Here E_i and A_i are defined by (4.7) and (4.13), respectively.

2. Reduction of $H'_+\psi' = E\psi'$

The reduction of Eq. (1.18) is in complete parallel with that of (1.19). Using Eq. (4.32) we write

$$\psi' = \mathcal{S}\psi'_P \tag{4.49}$$

with ψ'_P defined by

$$\psi'_P \equiv \mathcal{A}^{-1}\psi'^{(+)} . \tag{4.50}$$

The analogs of (4.36) and (4.37) are

$$\beta_i\psi'_P = \psi'_P \tag{4.51}$$

and

$$\mathcal{S}^\dagger\mathcal{S} = \beta_1^{(+)}\cdots\beta_N^{(+)} , \tag{4.52}$$

so that as in (4.38),

$$\langle\psi'|\psi'\rangle = \langle\psi'_P|\psi'_P\rangle . \tag{4.53}$$

The analog of (4.39) is

$$\mathcal{H}'^{\,\mathrm{red}}_+\psi'_P = E\psi'_P \tag{4.54a}$$

with

$$\mathcal{H}'^{\,\mathrm{red}}_+ \equiv \mathcal{S}^\dagger\mathcal{H}'_+\mathcal{S} . \tag{4.54b}$$

The relativistic SP-type Hamiltonian analogous to (4.40) is then

$$\mathcal{H}^{\mathrm{rel}}_P = \mathcal{H}'^{\,\mathrm{red}}_+\big|_{\beta_i\to 1,\ \vec{\sigma}_i^{\,p}\to\vec{\sigma}_i} \tag{4.55}$$

and the multi-Pauli spinor wave function

$$\psi_P = \psi_P(1,\ldots,N) \tag{4.56}$$

obtained by dropping the zero components of ψ'_P satisfies

$$\mathcal{H}^{\mathrm{rel}}_P\psi_P = E\psi_P . \tag{4.57}$$

A more explicit form of $\mathcal{H}^{\mathrm{rel}}_P$ may be obtained by using relations analogous to (4.43)

$$\mathcal{S}_i^\dagger\mathcal{O}_+\mathcal{S}_i = \mathcal{A}_i(\mathcal{O}_+ + \mathcal{R}_i^\dagger\mathcal{O}_+\mathcal{R}_i)\mathcal{A}_i\beta_i^{(+)} , \tag{4.58a}$$

$$\mathcal{S}_i^\dagger\mathcal{O}_-\mathcal{S}_i = \mathcal{A}_i(\mathcal{O}_-\mathcal{R}_i + \mathcal{R}_i^\dagger\mathcal{O}_-)\mathcal{A}_i\beta_i^{(+)} . \tag{4.58b}$$

These hold because $\mathcal{R}_i$ is β_i-even, like R_i, so that

$$\beta_i^{(+)}\mathcal{R}_i\beta_i^{(+)} = 0 . \tag{4.59}$$

To describe the result some new notation is needed. The Pauli equivalent $\hat{\mathcal{R}}_i$ of $\mathcal{R}_i$ is defined by deleting ρ_i in (4.25) and replacing $\vec{\sigma}_i^{\,p}$ by $\vec{\sigma}_i$. Thus

$$\hat{\mathcal{R}}_i \equiv [\hat{a}_i - \hat{b}_i + m + eA^0_{\mathrm{ext}}(i)]^{-1} \times(\vec{\sigma}_i\cdot\vec{\Pi}_i - \hat{c}_i + \hat{d}_i) , \tag{4.60}$$

with, e.g. [see (4.23)],

$$\hat{a}_i \equiv a_i^{(0)} + \vec{\sigma}_i\cdot\vec{a}_i^{(1)} . \tag{4.61}$$

Similarly, the Pauli equivalent $\hat{\mathcal{A}}_i$ of $\mathcal{A}_i$ is defined [see (4.31)] by

$$\hat{\mathcal{A}}_i \equiv (1 + \hat{\mathcal{R}}_i^\dagger\hat{\mathcal{R}}_i)^{-1/2} . \tag{4.62}$$

Let us denote the Pauli equivalent of $\mathcal{H}^{\mathrm{red}}_{D;\,\mathrm{ext}}(i)$ by $\mathcal{E}_P(i)$

$$\mathcal{E}_P(i) \equiv [\mathcal{S}_i^\dagger\mathcal{H}_{D;\,\mathrm{ext}}(i)\mathcal{S}_i]_{\beta_i\to 1,\ \vec{\sigma}_i^{\,p}\to\vec{\sigma}_i} . \tag{4.63}$$

Using these definitions and the relations (4.28) and (4.58) we find that

$$\mathcal{E}_P(i) = \hat{\mathcal{A}}_i\{\vec{\sigma}_i\cdot\vec{\Pi}_i\hat{\mathcal{R}}_i + \mathrm{H.c.} + m + eA^0_{\mathrm{ext}}(i) + \hat{\mathcal{R}}_i^\dagger[-m + eA^0_{\mathrm{ext}}(i)]\hat{\mathcal{R}}_i\}\hat{\mathcal{A}}_i , \tag{4.64}$$

and the Pauli equivalent $\mathcal{V}^{\mathrm{rel}}_P(i,j)$ of $(e^2/r_{ij} + B_{ij})^{\mathrm{red}}$ can be similarly found. Thus we get

$$\mathcal{H}^{\mathrm{rel}}_P = \sum_i \mathcal{E}_P(i) + \sum_{i<j}\mathcal{V}^{\mathrm{rel}}_P(i,j) , \tag{4.65}$$

where

$$\mathcal{V}^{\mathrm{rel}}_P(i,j) = \hat{\mathcal{A}}_i\hat{\mathcal{A}}_j\left(\frac{e^2}{r_{ij}} + \hat{\mathcal{R}}_i^\dagger\frac{e^2}{r_{ij}}\hat{\mathcal{R}}_i + \hat{\mathcal{R}}_j\frac{e^2}{r_{ij}}\hat{\mathcal{R}}_j + \hat{\mathcal{R}}_i^\dagger\hat{\mathcal{R}}_j^\dagger\frac{e^2}{r_{ij}}\hat{\mathcal{R}}_i^\dagger\hat{\mathcal{R}}_j^\dagger\right)\mathcal{A}_i\mathcal{A}_j + \mathcal{A}_i\mathcal{A}_j(\hat{B}_{ij}\hat{\mathcal{R}}_i\hat{\mathcal{R}}_j + \hat{\mathcal{R}}_i^\dagger\hat{B}_{ij}\hat{\mathcal{R}}_j + \hat{\mathcal{R}}_j^\dagger\hat{B}_{ij}\hat{\mathcal{R}}_i + \hat{\mathcal{R}}_i^\dagger\hat{\mathcal{R}}_j^\dagger\hat{B}_{ij})\mathcal{A}_i\mathcal{A}_j . \tag{4.66}$$

The nonrelativistic limits of $\mathcal{H}^{\mathrm{rel}}_P$ and h^{rel}_P are discussed in Appendix B, together with some techniques for simplifying the operators $\hat{\mathcal{R}}_i$, $\hat{\mathcal{A}}_i$, and $\mathcal{E}_P(i)$.

V. SUMMARY AND DISCUSSION

In Secs. IIA and IIB, two alternative Hamiltonians, each suitable as a starting point for the calculation of relativistic effects in an N-electron atom, were derived from QED. Unlike the Dirac-Coulomb Hamiltonian $\mathcal{H}_{\mathrm{DC}}$, the operators $\mathcal{H}_+$ and h_+, defined by Eqs. (1.8) and (1.9), respectively, can be expected to have normalizable eigenfunctions corresponding to the discrete part of the atomic spectrum. The operator $\mathcal{H}_+$ is just the configuration space equivalent of the "no-pair" matter Hamiltonian $H^{\mathrm{np}}_{\mathrm{mat}}$ in the N-electron sector of Fock space. In Sec. IIC it was shown how the field-theoretic origin of $\mathcal{H}_+$ allows one to go further and to write down in a simple manner expressions for transition amplitudes involving real photons and for level shifts arising from the effects of virtual photons and virtual electron-positron pairs, in terms of the residual part $H' = H_T + H^{\mathrm{pair}}_{\mathcal{C}}$ of the full Ham-

iltonian—no new questions of principle arise. The leading terms in the one-photon transition amplitude and in the level-shift are expressible completely in terms of the eigenfunctions of $\mathcal{H}_+$. Similar remarks hold for h_+. Another feature of the Hamiltonians $\mathcal{H}_+$ and h_+ is that the first-order effect as well as some of the higher-order effects of photon-exchange between electrons can be included by adding the Breit operator B_{ij} to e^2/r_{ij} in $\mathcal{H}_+$ and in h_+, leading to modified Hamiltonians $\mathcal{H}'_+$ and h'_+ given by (2.37) and (2.38). Because of the projection operators $\mathcal{L}_+$ or Λ_+ no spuriously large terms are generated thereby.

A Hartree-Fock approximation to an eigenfunction ψ of $\mathcal{H}_+$ was defined in Sec. III and relativistic HF equations for the associated Dirac-spinor orbitals $\psi_i(1)$ were obtained. These equations are similar in form to the DHF equations based on $\mathcal{H}_{DC}$, except for two projection-operator factors between which the operators associated with the electron-electron interactions and with exchange are sandwiched. It was shown that the orbitals χ_i associated with the DHF wave function χ can be regarded as approximations to the ψ_i, so that χ can be interpreted as an approximation to ψ^{HF} and hence to ψ itself, a function which has a clear-cut theoretical significance within the framework of QED. Relativistic HF equations associated with the other no-pair Hamiltonians h_+, $\mathcal{H}'_+$, and h'_+ were also derived.

In Sec. IV, the reduction of the Dirac-like equations $\mathcal{H}'_+\psi' = E\psi'$ and $h'_+\phi' = E\phi'$ to equations for suitably defined Pauli-type wave functions ψ_P and ϕ_P was carried out. This could be done in closed form, without the use of operators which depend on the energy E as a parameter. The resulting equations (4.57) and (4.42) involving the relativistic Pauli-type Hamiltonians $\mathcal{H}_P^{\mathrm{rel}}$ and h_P^{rel} given by Eqs. (4.65) and (4.44) are therefore not only linear but still fully equivalent to the original equations involving $\mathcal{H}'_+$ and h'_+. The major advantage of the reduced equations over the original equations is that the constraints $\mathcal{L}_+(i)\psi' = \psi'$ and $\Lambda_+(i)\phi' = \phi'$ have been eliminated; correspondingly, the wave functions ψ_P and ϕ_P have only 2^N (unconstrained) components, as in the nonrelativistic case. The HF equations associated with h_P^{rel} are described in Appendix A. The nonrelativistic limit of the no-pair equations is discussed in Appendix B; some approximation techniques which may be useful in applications are also described there. We now consider further a number of aspects and implications of the results summarized above.

A. Comparison of relativistic Hamiltonians

When the electron-electron interaction is switched off both $\mathcal{H}_+$ and $\mathcal{H}'_+$ become equal to

$$\mathcal{H}_+^{(0)} \equiv \sum_i \mathcal{H}_{D;\,\mathrm{ext}}(i) = \sum_i [\mathcal{H}_D(i) + V_{\mathrm{ext}}(i)] \tag{5.1}$$

whereas h_+ or h'_+ become equal to

$$h_+^{(0)} = \sum_i \mathcal{H}_D(i) + \Lambda_+ \sum_i V_{\mathrm{ext}}(i)\Lambda_+ \,. \tag{5.2}$$

Because $\Lambda_+(i)\phi = \phi$, $h_+^{(0)}$ is equivalent to

$$H_+^{(0)} = \sum_i \mathcal{H}_+(i)\,, \tag{5.3}$$

where

$$\mathcal{H}_+(i) = \mathcal{H}_D(i) + \Lambda_+(i)V_{\mathrm{ext}}(i)\Lambda_+(i)\,. \tag{5.4}$$

It can be shown that the eigenvalues of $\mathcal{H}_+(i)$ differ from those of $\mathcal{H}_{D;\,\mathrm{ext}}(i)$ by terms of order $\langle p^2 V_{\mathrm{ext}}^2/m^3\rangle$, which for $V_{\mathrm{ext}} = Z\alpha/r$ are of order $(\alpha Z)^6 m = (\alpha Z)^4(Z^2\mathcal{R})$. The reasons for this difference is that whereas the approach based on the external-field expansion of the Dirac field $\psi_D(\bar{x})$ becomes exact if H_C (and H_T) are switched off, the free-field expansion leaves over a term $H_{\mathrm{ext}}^{\mathrm{pair}}$ which must still be taken into account. The leading effect of $H_{\mathrm{ext}}^{\mathrm{pair}}$ may be computed by using second-order perturbation theory and neglecting lepton recoil energies in the intermediate states, which contain not only the initial electron but also an electron-positron pair. One then finds a contribution which precisely accounts for the $O((\alpha Z)^6)$ difference between the eigenvalues of $\mathcal{H}_+(i)$ and $\mathcal{H}_{D;\,\mathrm{ext}}(i)$.

From this discussion it follows that within the framework of an HF approximation to the eigenfunctions ψ and ϕ of $\mathcal{H}'_+$ and h'_+, the single-electron energies ϵ'_i and $\bar{\epsilon}'_i$ associated with orbitals ψ'_i and ϕ'_i will only differ by terms of order $\alpha^6 m$ for high-lying orbitals and by terms of order $(\alpha Z)^6 m$ for the innermost orbitals. One can therefore conclude that the energy differences between states that correspond to one-electron excitations as computed from h'_+ will not differ appreciably from those computed from $\mathcal{H}'_+$.

B. Practical aspects

The advantage of the "$\mathcal{H}$-type" Hamiltonians $\mathcal{H}^+$ or $\mathcal{H}'_+$ over the "h-type" Hamiltonians h_+ or h'_+ of being exact in the limit $V_{\mathrm{ext}} \gg V_{\mathrm{ee}}$, is balanced by the fact that the h-type operators are much simpler to work with. This is because, in momentum space, the projection operator $\Lambda_+(i)$ is just an algebraic function of $\vec{p}_i$ whereas $\mathcal{L}_+(i)$ is a complicated operator even in momentum space. In particular, the HF equations for the orbitals associa-

ted with an HF approximation to an eigenfunction ϕ' of h'_+ are no more complicated, *in momentum space*, than the DHF equations for the orbitals $\chi_i(1)$.

This feature of the equation for ϕ' is preserved on passage to the reduced equations for the Pauli wave function ϕ_P

$$h_P^{\rm rel}\,\phi_P = E\phi_P\,, \tag{5.5}$$

where $h_P^{\rm rel}$ is given by Eq. (4.44). The operator $h_P^{\rm rel}$ has the following properties. (i) In an expansion in powers of $\vec{\mathrm{p}}_i^{\,2}/m^2$ it has the form

$$h_P^{\rm rel} = H_{\rm nr} + H_{\rm fs} + \cdots\,, \tag{5.6}$$

where $H_{\rm nr}$ is the completely nonrelativistic Hamiltonian for N electrons and $H_{\rm fs}$ is the usual operator for, e.g., spin-spin, spin-orbit, and orbit-orbit interactions, responsible for atomic fine structure. The dots in (5.6) represent operators which give rise to level shifts of order $(\alpha Z)^6 m$ or smaller. (ii) The full operator $h_P^{\rm rel}$ is, in momentum space, *no more complicated* than the operator $H_{\rm nr} + H_{\rm fs}$.

It follows, in particular, that in momentum space the HF equations corresponding to $h_P^{\rm rel}$ for the orbitals associated with the Pauli function ϕ_P, given in Appendix A, are basically no more complicated than are the DHF equations. In fact, they should be easier to solve numerically, because a multi-Pauli spinor has only 2^N components in contrast to a multi-Dirac spinor which has 4^N components.

C. Concluding remarks

The equations given in this paper can be used as the starting point for the investigation of relativistic effects in the spectra and transition probabilities in many-electron atoms. Because they are derived from field theory, no questions of principle arise in their use. The Hamiltonian $h_P^{\rm rel}$ leads to HF-type equations which are, in momentum space, simpler than the DHF equations and therefore it should be possible to use $h_P^{\rm rel}$ as a basis for calculations which are both practical and securely grounded in quantum electrodynamics.

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APPENDIX A: HF APPROXIMATIONS FOR $h_p^{\rm rel}$ AND $H_p^{\rm rel}$

The relativistic HF equations based on h'_+, which includes the Breit interaction, are given by Eq. (3.13) of Sec. III of the text. In these equations the orbitals $\phi'_i(1)$ are still subject to the positive-energy constraint (3.15), which may be awkward to implement in numerical calculations. However, this constraint can be eliminated by using the reduction techniques described in Sec. IV. Equivalently, and more simply, one may instead derive the reduced HF equations directly, by making an HF approximation to

$$h_P^{\rm rel}\,\phi_P = E\phi_P\,, \tag{A1}$$

where ϕ_P is the Pauli wave function associated with ϕ' and $h_P^{\rm rel}$ is the relativistic Schrödinger-Pauli-type Hamiltonian defined by (4.44). With the trial function

$$\phi_P^{\rm HF} = (1/\sqrt{N!})\,\mathrm{Det}[\varphi_1(1)\varphi_2(1)\cdots\varphi_N(1)] \tag{A2}$$

and $\varphi_i(1)$ a Pauli wave function (spin orbital), the variational principle applied to (A1) gives

$$E(\vec{\mathrm{p}}_1)\varphi_i(1) + V_i^{\rm rel}(1)\varphi_i(1) - \sum_{j\neq i} U_{ji}^{\rm rel}(1)\varphi_j(1) = \sum_j \lambda_{ij}\varphi_j(1)\,, \tag{A3}$$

where

$$U_{ij}^{\rm rel}(1) = \langle\varphi_i(2)|\,V^{\rm rel}(1,2)\,|\varphi_j(2)\rangle \tag{A4}$$

and

$$V_i^{\rm rel}(1) = V_{\rm ext}^{\rm rel}(1) + \sum_{j\neq i} U_{jj}^{\rm rel}(1)\,. \tag{A5}$$

Here $V^{\rm rel}(1,2)$ and $V_i^{\rm rel}(1)$ are given by Eqs. (4.47) and (4.45) of the text, respectively, and the λ's are the Lagrange multipliers associated with the constraint $\langle\varphi_i|\varphi_j\rangle = \delta_{ij}$.

Note that no projection operators appear in (A3). Apart from kinematical factors of the form $\{[E(\vec{\mathrm{p}})+m]/2E(\vec{\mathrm{p}})\}^{1/2}$ and $2m/[E(\vec{\mathrm{p}})+m]$ which enter the definitions of $V^{\rm rel}(1,2)$ and $V_{\rm ext}^{\rm rel}(1)$, (A3) has the form one would get for the HF equations based on the nonrelativistic SP Hamiltonian $H_{\rm nr}+H_{\rm fs}$, where $H_{\rm fs}$ contains the nonrelativistic fine-structure operators. In momentum space, these kinematical factors are slowly varying functions which would be simple to incorporate in numerical calculations.

The HF equations based on $\mathcal{H}'_+$, given by (3.12), may similarly be reduced to SP form and the constraint $\mathcal{E}_+(1)\psi' = \psi'$ eliminated, by applying the variational principle directly to the equivalent relativistic SP equation (4.57). With a trial function of the form (A2) one gets

$$\mathcal{E}_P(1)\varphi_i(1) + \sum_{j\neq i}\mathfrak{u}_{jj}^{\rm rel}(1)\varphi_i(1) - \sum_{j\neq i}\mathfrak{u}_{ji}^{\rm rel}(1)\varphi_j(1) = \sum_j \lambda_{ij}\varphi_j(1)\,, \tag{A6}$$

where $\mathcal{E}_P(1)$ is defined by (4.64) and

$$\mathfrak{u}_{ij}^{\rm rel}(1) = \langle \varphi_i(2) | \mathfrak{v}_P^{\rm rel}(1,2) | \varphi_j(2) \rangle , \tag{A7}$$

with $\mathfrak{v}_P^{\rm rel}(1,2)$ defined by (4.66). However, because of the complicated character of some of the operators entering the definition of $\mathcal{E}_P$ and $\mathfrak{v}_P^{\rm rel}$, further approximations will have to be made before (A6) becomes amenable to numerical solution. [For an example, see Eq. (B11).]

APPENDIX B: NONRELATIVISTIC LIMITS

The nonrelativistic limit of $h_P^{\rm rel}$ is easily found, by expansion of the operators A_i and $\hat{R}_i$ in powers of $p_i/m = O(v/c)$. Using

$$\begin{aligned} A_i &= 1 + (\vec{\mathfrak{p}}_i^2/8m^2) + O(v^4/c^4) , \\ R_i &= (\vec{\sigma}_i \cdot \vec{\mathfrak{p}}_i/2m)[1 - (\vec{\mathfrak{p}}_i^2/4m^2) + O(v^4/c^4)] , \end{aligned} \tag{B1}$$

one gets

$$\begin{aligned} V_{\rm ext}^{\rm rel}(i) = &-eA_{\rm ext}^0(i) + \frac{e}{2m}[\vec{\mathfrak{p}}_i \cdot \vec{A}_{\rm ext}(i) + \text{H.c.}] \\ &+ \frac{e}{2m}\vec{\sigma}_i \cdot \vec{H}_{\rm ext}(i) + \frac{e}{4m^2}\vec{\sigma}_i \cdot \vec{E}_{\rm ext}(i) \times \vec{\mathfrak{p}}_i \\ &- \frac{e}{8m^2}[\vec{\mathfrak{p}}_i \cdot, [\vec{\mathfrak{p}}_i, A_{\rm ext}^0(i)]_+]_+ + \cdots , \end{aligned} \tag{B2}$$

where the dots represent terms of order $(v^4/c^4)A_{\rm ext}^0$ and $(v^3/c^3)|\vec{A}_{\rm ext}|$ or higher. The first four terms in (B2) are familiar. The double anticommutator term combines with the $\vec{\mathfrak{p}}^4$ term in the expansion of E_i,

$$E_i = m + \vec{\mathfrak{p}}_i^2/2m - \vec{\mathfrak{p}}_i^4/8m^3 + \cdots , \tag{B3}$$

to give a spin-independent interaction, responsible for the leading relativistic correction to S-state levels in one-electron atoms. Similarly, one finds

$$\begin{aligned} V^{\rm rel}(i,j) = &\frac{e^2}{r_{ij}} + V_{\rm oo}(i,j) + V_{\rm so}(i,j) \\ &+ V_{\rm ss}(i,j) + O\left(\frac{v^4}{c^4}\frac{e^2}{r_{ij}}\right) \end{aligned} \tag{B4}$$

where $V_{\rm oo}$, $V_{\rm so}$, and $V_{\rm ss}$ are the usual orbit-orbit, spin-orbit and spin-spin interaction operators. Thus $h_P^{\rm rel}$ contains all the familiar fine-structure operators, together with corrections of higher order in v/c.

The same statement holds for $\mathcal{K}_P^{\rm rel}$, given by (4.65). To verify this, it is convenient to "mechanize" the formal definition (4.18) of $\mathcal{E}(i)$,[16] by noting that $\mathcal{E}(i)$ may be thought of as the positive square root of $\mathcal{K}_{D;\rm ext}(i)$:

$$\mathcal{E}(i) = [\mathcal{K}_{D;\rm ext}^2(i)]^{1/2} . \tag{B5}$$

One can expand the square root in powers of m^{-1},

$$\begin{aligned} \mathcal{E}(i) &= m(1 + Q_i)^{1/2} \\ &= m(1 + \tfrac{1}{2}Q_i - \tfrac{1}{8}Q_i^2 + \cdots) , \end{aligned} \tag{B6}$$

where

$$Q_i \equiv (\mathcal{K}_{D;\rm ext}^2(i) - m^2)/m^2 . \tag{B7}$$

When this expansion is used together with similar expansions in m^{-1} for the operators $\hat{\mathcal{R}}_i$ and $\hat{\mathcal{Q}}_i$ entering (4.65), one finds that $\mathcal{K}_P^{\rm rel}$ has the same form as $h_P^{\rm rel}$ through terms of order $(v^4/c^4)m$, $(v^2/c^2)A_{\rm ext}^0$, $(v^2/c^2)(e^2/r_{ij})$, and $(v/c)|\vec{A}_{\rm ext}|$.

It is possible to expand $\mathcal{E}(i)$ in powers of $A_{\rm ext}^\mu(i)$ only, without expanding in powers of $\vec{\mathfrak{p}}_i/m$ at the same time. One may write

$$\mathcal{E}(i) = (a_i + b_i)^{1/2} \tag{B8}$$

with

$$\begin{aligned} a_i &= m^2 + \vec{\mathfrak{p}}_i^2 , \\ b_i &= \vec{\Pi}_i^2 - \vec{\mathfrak{p}}_i^2 - e[\vec{\alpha}_i \cdot \vec{\Pi}_i + \beta_i m, A_{\rm ext}^0(i)]_+ \\ &\quad + e^2[A_{\rm ext}^0(i)]^2 . \end{aligned}$$

Now for any operators a and b, one has

$$(a+b)^{1/2} = \frac{1}{2\sqrt{\pi}} \int_0^\infty du (1 - e^{-u(a+b)}) u^{-3/2} , \tag{B9}$$

and Feynman's operator calculus[17] can be used to expand $e^{-u(a+b)}$ in a power series in b. On computation one finds[18]

$$\begin{aligned} (a+b)^{1/2} = a^{1/2} + \frac{1}{2\sqrt{\pi}} &\int_0^\infty du\, u^{-1/2} \\ &\times \int_0^1 ds\, e^{-aus} b e^{-au(1-s)} + \cdots . \end{aligned} \tag{B10}$$

With $a = a_i$, $b = b_i$ we then get from (B9) and (B10)

$$\mathcal{E}(i) = E_i + \frac{1}{2\sqrt{\pi}} \int_0^\infty du\, u \int_0^1 ds\, e^{-(1-s)uE_i} b_i e^{-suE_i} + \cdots . \tag{B11}$$

For $\vec{A}_{\rm ext} = 0$ and $A_{\rm ext}^0(b) = Ze/r_i$, replacement of b_i by $-2Z\alpha\beta_i m/r_i$ in (B11) gives the leading $O(Z\alpha m)$ correction to the zeroth-order approximation $\mathcal{E}(i) \approx E_i$. The expansion (B11), which has been used in a study of the $\alpha^3\mathcal{R}$ corrections to the energy levels of helium,[3] may also prove useful in the calculation of relativistic effects in many-electron atoms. It is, roughly speaking, an expansion in powers of $mZ\alpha r_i^{-1}/E_i^2$, which is likely to converge more rapidly than an expansion in powers of $Z\alpha r_i^{-1}/m$. Similar expansions can be given for all the operators which enter the definition of $\mathcal{K}_P^{\rm rel}$.

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[11]Renormalization counter terms which must be added to the right-hand side of (2.1) are suppressed throughout.

[12]In our definition of $H_{\mathcal{C}}^{\mathrm{pp}}$ we also replace an operator such as $(A_1^\dagger A_2 A_3^\dagger A_4)$ by its normal-order form $(-A_1^\dagger A_3^\dagger A_2 A_4)$. The difference between these forms corresponds to part of the electron-Coulomb self-energy. This difference ultimately must be treated together with the self-energy effects coming from H_T in order to be able to carry out mass renormalization when one calculates radiative corrections.

[13]For a discussion of these spurious effects, see H. A. Bethe and E. C. Salpeter, *Quantum Theory of One- and Two-Electron Atoms* (Academic, New York, 1978), pp. 170–178. However, the difficulty with the spectrum of $\mathcal{H}_{\mathrm{DC}}$ is not mentioned there.

[14]An explanation of the terminology associated with HF approximation schemes may be found in C. Froese Fischer, *The Hartree-Fock Method for Atoms* (Wiley, New York, 1977), pp. 13–16.

[15]J. Sucher, Phys. Rev. 103, 468 (1956). The word "small" in the abstract of this paper should read "large."

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[17]R. P. Feynman, Phys. Rev. 84, 108 (1951).

[18]J. Sucher, J. Math. Phys. 4, 17 (1963).