Comments

Comment on relativistic wave equations and negative-energy states

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In a recent article [Phys. Rev. A **30**, 703 (1984)] Hardekopf and Sucher solve the relativistic wave equation in momentum space for hydrogenlike systems. They find that by surrounding the hydrogenic Hamiltonian with projection operators for free-particle positive-energy states, the ground-state energy is lowered. In this Comment, we investigate this problem in some detail and conclude that the application of unsuitable projection operators will, in fact, *introduce* negative-energy states to the Hamiltonian of interest rather than remove them. The general considerations lead to the conclusion that in studying single-particle *corrections* to the wave function in a perturbation expansion, the correct procedure is to include the negative-energy states of the unperturbed Hamiltonian. It is also noted that the use of relativistic Hartree-Fock wave functions will remove to lowest order of perturbation theory the presence of single virtual electron-positron pairs.

I. INTRODUCTION

The Dirac Hamiltonian

$$h_D = (\beta mc^2 + c\alpha \cdot \mathbf{p} - Ze^2/4\pi\epsilon_0 r) \tag{1}$$

gives both positive- and negative-energy solutions.[1] To explain why electrons in the real world show no intention of disappearing into the negative continuum, the negative states are considered as being filled under "normal conditions." This property is, however, not included in the Dirac equation, which causes problems if the equation is extended to the many-body case. The relativistic analogue to the many-body Schrödinger equation

$$H\Psi = \left[\sum_i h_D(i) + \frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \right] \Psi = E\Psi \tag{2}$$

has no normalizable eigenfunctions, as first pointed out a long time ago by Brown and Ravenhall.[2] As emphasized, e.g., by Sucher[3,4] the solution provided by quantum electrodynamics (QED) is to surround the Hamiltonian in (1) by projection operators, Λ^+, which force the electrons to stay in the positive part of the energy spectrum;

$$H^+\Psi^+ = \Lambda^+ \left[\sum_i h_D(i) + r_{12}^{-1} \right] \Lambda^+ \Psi^+ = E^+\Psi^+ . \tag{3}$$

(Here and throughout the rest of the paper we have used atomic units, where $\hbar = 4\pi\epsilon_0 = a_0 = m_e = 1$. We have also used the convention that lower case refers to one electron and upper case to the whole system.) The projection operators Λ^+ for positive-energy states are easily written in terms of products of one-particle projection operators λ_i^+,

$$\lambda_i^+ = \sum_{\substack{n \\ (\epsilon_n > 0)}} |\phi_n(i)\rangle\langle\phi_n(i)| = \sum_n^{\text{pos}} |n^+\rangle\langle n^+| ,$$

but less easy to implement in an actual calculation.

In a recent paper, Hardekopf and Sucher[5] solve the rel-

ativistic wave equation in momentum space and include projection operators for plane-wave positive-energy states. However, they observe that for hydrogenlike systems the energy is always lower than the exact $1s$ energy. It thus appears that by attempting to remove the negative-energy states, the reverse has been achieved. This problem is investigated in some detail in Sec. II C.

While the problems connected with the two-body (or many-body) equations are severe and fundamental and deserve careful treatment, the present work deals only with one-particle equations, where any problems with negative-energy states are related to the method used to obtain a solution rather than inherent in the one-particle equation itself. However, the validity of the commonly used relativistic Hartree-Fock (HF) approximation

$$H^{\text{HF}} = \sum_i h^{\text{HF}} = \sum_i (h_D + v^{\text{HF}}) , \tag{4}$$

with

$$v^{\text{HF}}|a\rangle = \sum_b^{\text{occ}} (\langle b|r_{12}^{-1}|b\rangle|a\rangle - \langle b|r_{12}^{-1}|a\rangle|b\rangle)$$

$$= \sum_b^{\text{occ}} \langle b|r_{12}^{-1}(1-P_{12})|b\rangle|a\rangle \tag{5}$$

has also been questioned,[3,4] since it is normally derived by minimizing the expectation value of the Hamiltonian (2) without any explicit inclusion of projection operators.

It is well known that the solution of the full many-body Hamiltonian, containing the interelectron interaction, cannot be separated into one-particle wave functions. In reality a particular state of a system is described by only one many-electron wave function and one total energy. Within the single-particle approximation certain eigenstates to our approximate one-particle Hamiltonian can be classified as having negative-energy eigenvalues and may be rejected if desired, whereas there is no easy way to tell from the total energy of the system if anything unwanted is included or not. This means that the projection operator has to be expressed in terms of some one-particle basis. In principle any basis set could be chosen. If we really

solve the whole problem, including also corrections coming from virtual pairs, the solution should be projection-operator independent. However, the so-called no-pair approximation, which is the approximation used in practice when dealing with atoms with more than a few electrons, does depend on the choice.[6]

Sucher claims[3,4] that a good choice of projection operators is given by solutions in the positive-energy range of the free-particle Hamiltonian. For heavier atoms he follows Furry[7] and suggests the use of hydrogenlike projection operators. Mittleman has shown[8] that starting from the projected Hamiltonian (3) and looking for the projection operator Λ^+ which makes the energy stationary under the condition that the wave function should consist of a single Slater determinant, leads to a Λ^+ given exactly by HF projection operators. Thus, the relativistic HF equations can be considered as an approximation to (3) rather than to (2). An alternative proof of the fact that the solutions to the unprojected HF equations are solutions also to the projected HF equation is given in Sec. II B in a language more familiar to atomic physicists.

II. GENERAL OBSERVATIONS

A. The positive-energy states of a one-particle Hamiltonian

When a one-particle eigenvalue equation, $(\varepsilon_0 - h_0) | a_0 \rangle = 0$, is *solved* for an arbitrary one-body Hamiltonian h_0, the negative-energy states, if ever generated, are easily rejected by inspection of the energy value. A positive-energy solution $| a_0^+ \rangle$ does not contain any negative component $| a_0^- \rangle$ since eigenfunctions to an Hermitian operator corresponding to different eigenvalues are orthogonal. Thus insertion of a projection operator $\lambda^+ = \sum_i^{pos} | i_0^+ \rangle \langle i_0^+ |$ has no effect on $| a_0^+ \rangle$ and if h_0 is replaced by a projected Hamiltonian $h_0^+ = \lambda^+ h_0 \lambda^+$, the positive-energy states remain unchanged. The only difference is that the negative-energy states are not generated and that *the projected Hamiltonian no longer has a complete set of eigenfunctions.*

It can be noted, however, that minimization of the expression $\langle a | h_0 | a \rangle / \langle a | a \rangle$ within an incomplete finite basis set may lead to negative or too low energies,[9] although the difficulty can be circumvented by requiring certain relations between the basis sets used to describe the upper and lower components of the wave function as discussed by Grant and co-workers.[10]

B. The positive-energy states in relativistic Hartree-Fock theory

The argument in Sec. II A may be applied also to the relativistic Hartree-Fock approximation (4) and (5) although there is more room for confusion in this case. In general, $\langle i^- | v^{HF} | a^+ \rangle \neq 0$. Thus, the HF potential defined by (5), above, is different from a projected HF potential, where r_{12}^{-1} is surrounded by projection operators. One finds

$$v_{proj}^{HF} | a_1 \rangle = \sum_b^{occ} b \left\langle b_2 \left| \lambda_1^+ \lambda_2^+ \frac{1}{r_{12}} \lambda_2^+ \lambda_1^+ (1 - P_{12}) \right| b_2 \right\rangle | a_1 \rangle$$

$$= \lambda_1^+ \sum_b^{occ} \left\langle b_2 \left| \frac{1}{r_{12}} (1 - P_{12}) \right| b_2 \right\rangle | a_1 \rangle$$

$$= v^{HF} | a_1 \rangle - \sum_i^{neg} | i_1^- \rangle \langle i_1^- | v^{HF} | a_1 \rangle ,$$

where we have used the fact that $\lambda^+ | a \rangle = | a \rangle$ for $\varepsilon_a > 0$ if λ^+ is expressed in orbitals obtained in the same potential as $| a \rangle$. (This is a natural choice in an iterative procedure, since the best approximation available for λ^+ is based on orbitals obtained in the previous iteration.) To compensate for the difference between the projected and unprojected HF potentials it is necessary to surround also h_D in (4) by HF projection operators (although these are only implicitly included in the equations given by Sucher[3-5]). However, from $\langle a^- | h^{HF} | i^+ \rangle = 0$, where $| a^- \rangle$ and $| i^+ \rangle$ are eigenfunctions to h^{HF} given in (4) and (5), follows that $\langle i^- | h_D | a^+ \rangle = - \langle i^- | v^{HF} | a^+ \rangle$ so the absence of projection operators in one part of the Hamiltonian is exactly canceled by the absence in the second part. Following the same arguments as above we find that a positive-energy solution $| a^+ \rangle$ to the equation $(\varepsilon_a^{HF} - h^{HF}) | a^+ \rangle = 0$ contains no negative-energy component, $| i^- \rangle$. From this discussion it should be obvious that the absence of negative-energy states in $| a_{HF}^+ \rangle$ is a direct consequence of a positive-energy eigenvalue ε_a and does not depend on subtle details in the solution procedure.

The arguments cannot be directly applied to the multiconfiguration Dirac-Fock method,[11] except when all configurations are expressed in terms of one single basis set, as discussed by Sucher in Ref. 4.

C. Projection operators corresponding to another Hamiltonian than the orbitals

Consider now a positive-energy solution $| a_1 \rangle$ to a given Hamiltonian h_1. Applying a projection operator λ_2^+, corresponding to a second Hamiltonian h_2, to $| a_1 \rangle$ will not in general reproduce $| a_1 \rangle$ since, in general, $\langle i_2^- | a_1^+ \rangle \neq 0$. If we then expand this projected function in the eigenfunctions to the original Hamiltonian h_1, we find

$$\lambda_2^+ | a_1^+ \rangle = \sum_i^{pos} | i_2^+ \rangle \langle i_2^+ | a_1^+ \rangle$$

$$= \sum_j^{all} \sum_i^{pos} | j_1^\pm \rangle \langle j_1^\pm | i_2^+ \rangle \langle i_2^+ | a^+ \rangle ,$$

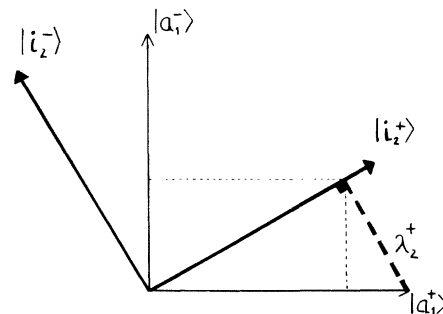where the completeness of the set $| j_1 \rangle$ has been used.

FIG. 1. Two-dimensional illustration of projection operators corresponding to different Hamiltonians. The horizontal axis corresponds to the set of positive-energy solutions $| a_1^+ \rangle$ to the Hamiltonian h_1 and the vertical axis to the orthogonal set of negative-energy solutions $| a_1^- \rangle$. The sets of positive- and negative-energy solutions to another Hamiltonian is represented by $| i_2^+ \rangle$ and $| i_2^- \rangle$. The projection of a positive-energy state $| a_1^+ \rangle$ onto the positive-energy states of h_2 is obtained by following the bold dashed line, thereby introducing a small admixture of the negative-energy state $| a_1^- \rangle$.

There is no reason for the coefficients for $|j_1^-\rangle$ to be zero in this sum. The situation is illustrated in Fig. 1. Thus by projecting with projection operator based on any Hamiltonian other than that used to generate the orbitals, *negative-energy eigenstates to the Hamiltonian of interest have been introduced rather than removed.* It is then not surprising that too low energy eigenvalues were obtained in Ref. 5.

D. The HF equations, perturbation theory, and negative energy states

The question of various basis sets is present when perturbation theory is applied to obtain solutions $|a\rangle$ to a Hamiltonian $h = h_0 + h^P$. Following Ref. 12 the equation $(\varepsilon_a - h)|a\rangle = 0$ can be rewritten as

$$(\varepsilon_a^0 + \delta\varepsilon_a - h_0)|a_0 + \delta a\rangle = h^P|a_0 + \delta a\rangle .$$

By requiring $\langle a_0 | \delta a\rangle = 0$, an expression for $\delta\varepsilon_a$ is obtained

$$\delta\varepsilon_a = \langle a_0 | h^P | a_0 + \delta a\rangle$$

and the equation above becomes

$$(\varepsilon_a^0 + \delta\varepsilon_a - h_0)|\delta a\rangle$$
$$= h^P|a_0 + \delta a\rangle - |a_0\rangle\langle a_0 | h^P | a_0 + \delta a\rangle$$
$$= \sum_{i_0(\neq a_0)} |i_0\rangle\langle i_0 | h^P | a_0 + \delta a\rangle , \qquad (6)$$

where the right-hand side has been rewritten using the closure relation. It is then clear that $|\delta a\rangle$ will contain negative-energy states $|i_0^-\rangle$ although their coefficients will, in general, be quite small due to the large energy denominator involved. We see that the positive-energy state $|a\rangle = |a_0 + \delta a\rangle$ no longer is orthogonal to the unperturbed negative-energy states. Similarly, the correction $|\delta n^-\rangle$ to a negative-energy state $|n^-\rangle$ will include admixtures of positive-energy eigenstates $|i_0^+\rangle$ to the unperturbed Hamiltonian. In this way the orthogonality between positive- and negative-energy states is still preserved. However, application of the unperturbed positive-energy projection operator λ_0^+ to the right-hand side of (6) will destroy this orthogonality and force $|a\rangle$ to contain part of the negative-energy states $|n_0^- + \delta n^-\rangle$ as observed also in Sec. II C and illustrated in Fig. 1. To summarize, *an exact solution to the perturbed Hamiltonian h cannot be obtained if the summation over negative-energy states to h_0 are not allowed.* This has recently been observed in a numerical calculation by Quiney *et al.*[13] who performed explicitly the summations over all states. The need to include negative-energy states has been pointed out also by Goldman and Drake.[14] The only important requirement is that $|a\rangle$ is a *positive*-energy eigenvalue solution to h, not that it can be expanded in positive eigenvalue solutions to any other Hamiltonian h_0. *The phrase "negative-energy state" has no well-defined meaning until the single-particle Hamiltonian has been specified.*

The orbital-modification procedure described and used by Garpman *et al.*[12] uses the above equations to obtain HF solutions from a set of orbitals obtained in a local potential v_0 by setting $h^P = v^{HF} - v_0$. The argument is, however, not restricted to this case, but can be applied also when h^P is an external perturbation. For weak perturbations it is sufficient to keep the lowest-order terms. With

$h_0 = h^{HF}$, one gets

$$(\varepsilon_a^{HF} - h^{HF})|\delta a\rangle$$
$$= (h^P + v^P)|a^{HF}\rangle - |a^{HF}\rangle\langle a^{HF}| h^P + v^P|a^{HF}\rangle$$
$$= \sum_{i(\neq a)} |i^{HF}\rangle\langle i^{HF}|(h^P + v^P)|a^{HF}\rangle , \qquad (7a)$$

where v^P is the correction in v^{HF} due to the change in the orbitals

$$v^P = \sum_b [\langle b | r_{12}^{-1}(1 - P_{12})|\delta b\rangle + \langle\delta b | r_{12}^{-1}(1 - P_{12})|b\rangle] . \qquad (7b)$$

Just as in (6) the right-hand side contains negative states in terms of the unperturbed Hamiltonian, but $|a^{HF} + \delta a\rangle$ can still be considered as a positive-energy solution of a generalized Hartree-Fock equation with h^P included in the one-body Hamiltonian. This elegant way of treating one-body perturbations was suggested by Sandars[15] in connection with the study of weak interactions and has been applied to that problem by several authors to this problem[16] as well as to hyperfine structure[17,18] and g_J factors.[19] It should also be possible to use Eq. (7) to treat the effect on the electron orbitals due to the Breit interaction,[20] h_B, as well, by choosing $h_0 = h^{HF}$ and $h^P = v^B = \langle b | h_B(1 - P_{12})|b\rangle|a\rangle$.

The procedure (7) is quite similar to the relativistic random-phase approximation.[21] It is also closely related to the method of summing all one-particle diagrams "to all orders" (i.e., one order of the perturbations, all orders in the electrostatic interaction), described in Ref. 12. When applying perturbation theory, normally only excited states would be allowed, although it is easy to show that the effects due to the admixture of all occupied orbitals cancel. However, in perturbation theory also the negative-energy states should then be excluded from the right-hand side of (7), corresponding to the application of the projection operator λ_0^+ expressed in terms of unperturbed HF orbitals. Solving Eq. (7) as it stands means that the projection operators are expressed in terms of the perturbed orbitals $|i^{HF} + \delta i\rangle$. Thus the methods are not completely equivalent and if the negative-energy states are excluded from the right-hand side of (7a), incorrect results are obtained, as observed in Ref. 13. To remove the discrepancy it is then necessary to include "virtual-pair correction" terms just as observed in the hydrogen calculation by Hardekopf and Sucher.[5]

III. THE NO-PAIR HAMILTONIAN AND THE HARTREE-FOCK EQUATIONS

Sucher writes his no-pair Hamiltonian in the form

$$H^+(U) = \sum_i [h(U) + \lambda^+(U)(V_{nuc} - U)\lambda^+(U)]$$
$$+ \frac{1}{2}\sum_{\substack{i,j \\ (i\neq j)}} \Lambda^+(U)V_{e\text{-}e}\Lambda^+(U) ,$$

where $h(U) = \beta mc^2 + c\alpha\cdot\mathbf{p} + U$ and V_{nuc} is the nuclear attraction. The projection operator is expressed in terms of eigenfunctions to $h(U)$ and $V_{e\text{-}e}$ is the electron-electron interaction. The choice of U most often used in actual calculations for larger systems is $U = V_{nuc} + v^{HF}$. For perturbation theory the equivalent form

$$H^+(U) = \Lambda^+(U) \left[\sum_i h(V_{\text{nuc}} + v^{\text{HF}}) + \left[\sum_{i(\neq j)} V_{e\text{-}e} - \sum_i v^{\text{HF}} \right] \right] \Lambda^+(U) \qquad (8)$$

is more convenient. Sucher[4] expresses concern that the virtual-pair correction due to $\delta U = V_{\text{nuc}} - U$ may be large unless $U = V_{\text{nuc}}$. However, there are also virtual-pair correction terms $V_{e\text{-}e}^{\text{pair}}$ due to $V_{e\text{-}e}$, and it is clear from (8) that the total virtual-pair corrections to take into account are the excitations due to $V_{e\text{-}e} - v^{\text{HF}}$. It is known from atomic many-body theory[22] that in first-order single excitations (i.e., creation of a single "particle-hole pair") due to $V_{e\text{-}e}$ cancel exactly those due to the potential correction term, as illustrated in Fig. 2. (If the restricted Hartree-Fock approximation is used, single excitations caused by a valence electron will still be present. Single excitations due to the Breit interaction will also be present, unless this is included together with the electrostatic interaction in the HF equations.) From the perturbation theory point of view, this is a more important criterion than the energy minimization, since it reduces the number of diagrams to be evaluated.[22] This property should hold also for excitations from the negative energy states, if these are defined through the HF Hamiltonian. Thus the Hartree-Fock approximation, for orbitals as well as for projection operators, should be a good—in some sense the best—starting point for calculations based on the no-pair Hamiltonian H^+.

IV. CONCLUSION

Every choice of projection operators divides the complete Dirac space into two halves. The division is dif-

FIG. 2. Single excitations due to the electron-electron interaction, $V_{e\text{-}e}$ (first and second diagrams) and due to the potential correction term (third diagram) cancel if the Hartree-Fock potential is used. A summation over all occupied orbitals is implied for the internal lines. Relation holds for all eigenstates $|i\rangle$ and $|j\rangle$ to the HF Hamiltonian in Eqs. (4) and (5)—also for orbitals with negative energy.

ferent for different choices of basis sets and thus of projection operators. The projection-operator dependence can only be removed when going beyond the "no-pair" approximation, allowing creation of virtual electron-positron pairs.

For atoms with more than a few electrons the exact problem cannot be solved—not even without QED effects—and a good starting point is essential. From the point of view of perturbation theory, the main advantage with the Hartree-Fock potential is not that it minimizes the energy but that it reduces the number of diagrams, since the potential correction term cancels exactly the "effective one-body interaction" due to the interelectronic interaction[22] and there are no "single excitations" (i.e., creation of a single particle-hole pair) in first order. This property should be welcome also in studying QED effects, since it applies to the negative-energy states, as well, if these are defined by the HF potential and all "pair-correction terms" (due to the creation of a single electron-positron pair) vanish in first order.

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