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Bethe-Goldstone Equations in Scattering Theory

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The use of a continuum Bethe-Goldstone equation, recently proposed by Mittleman, to describe electron scattering by an alkali atom, is generalized by introducing the concept of continuum Bethe-Goldstone equations of successively higher order. In analogy to a method recently used for calculating mean-value properties of atomic stationary states, this makes possible the computation of net increments of a scattering amplitude or phase shift in successively higher orders, defined so that the sum of all net increments to order N (for an N-particle system) is the exact amplitude or phase shift. Variational equations that might be used to solve a continuum Bethe-Goldstone equation of order n are derived. Solution of a system of inhomogeneous linear equations is combined with integration of an integro-differential equation similar to a continuum Hartree-Fock equation. The formalism should be applicable to elastic scattering of an external particle by any many-fermion system.

I. INTRODUCTION

THE concept of nth-order Bethe-Goldstone equations has recently been proposed as the basis for a systematic procedure for computing the correlation energy and other stationary state mean-value properties of many-electron atoms.[1,2] There is no difficulty, in principle, in applying the same method to other many-fermion systems, in particular to nuclei and to the electrons in solids and molecules, although computational details make applications to atomic electrons much simpler than to these other systems.

In the present paper, a further generalization of the Bethe-Goldstone equations will be proposed, in the form of a procedure allowing successive approximations to a scattering amplitude or phase shift for an external electron or nucleon interacting with a many-particle scattering system. For convenience, this will be described in terms of electron-atom scattering, but the formalism can equally well be applied to other many-particle systems.

The Bethe-Goldstone equations developed in nuclear theory,[3] following the work of Brueckner,[4] are the time-independent Schrödinger equations for pairs of particles embedded in the Fermi sea of the remaining N-2 particles of an N-particle system. The two-particle Bethe-Goldstone wave function is constrained to be orthogonal to N-2 specified occupied orbitals of the Fermi sea. It has recently been proposed by Mittleman[5] that this same approach can be used in scattering theory. In particular, scattering of an electron by an alkali atom can be approximated by a continuum Bethe-Goldstone wave function for the external and series electron, constrained to be orthogonal to the occupied orbitals of the closed shell atomic core. The wave function satisfies boundary conditions appropriate to one bound electron and one free electron of specified momentum.

An nth-order Bethe-Goldstone equation has been defined as the time-independent Schrödinger equation for n particles embedded in the Fermi sea of the remaining $N-n$ particles of an N-particle system.[1,2] For stationary states, this is most conveniently described in terms of the complete set of Slater determinants $\Phi_{ij\cdots}{}^{ab\cdots}$ obtained from some specified normalized reference state determinant,

$$\Phi_0 = \det\phi_1(1)\cdots\phi_N(N), \tag{1}$$

by replacing occupied orbitals ϕ_i, $i \leq N$, by orthonormal unoccupied orbitals ϕ_a, $a > N$, taken from a complete set. Then the ordinary (second-order) Bethe-Goldstone equation for pair (ij) is equivalent to a variational calculation with trial function

$$\Psi_{ij} = \Phi_0 + \sum_a \Phi_i{}^a c_i{}^a + \sum_b \Phi_j{}^b c_j{}^b + \sum_{ab} \Phi_{ij}{}^{ab} c_{ij}{}^{ab}. \tag{2}$$

A Bethe-Goldstone equation of order n, for n specified occupied orbital indices $ijk\cdots$, is equivalent to a variational calculation with a trial function that is a linear combination of Φ_0 and all Slater determinants whose subscript indices are a subset of $ijk\cdots$. For example, the wave function Ψ_{ijk} would be a linear combination of determinants Φ_0, $\Phi_i{}^a$, $\Phi_j{}^b$, $\Phi_k{}^c$, $\Phi_{ij}{}^{ab}$, $\Phi_{ik}{}^{ac}$, $\Phi_{jk}{}^{bc}$, $\Phi_{ijk}{}^{abc}$, where indices ijk are fixed but abc take on all possible values. With this definition, the Bethe-Goldstone equation of order N is just the N-particle Schrödinger equation.

A stationary-state property of an N-particle system, defined by the mean value of some operator F, can be expressed as a sum of the net increments of this mean value obtained from Bethe-Goldstone wave functions of successively higher order. Let the matrix elements of F in the complete basis of Slater determinants be denoted by $F_{\mu\nu}$ .Then the gross increment of F, computed for Bethe-Goldstone wave function $\Psi_{ij\ldots}$, of order n, is

$$\Delta F_{ij\ldots} = \sum_\mu \sum_\nu (F_{\mu\nu} - \delta_{\mu\nu} F_{00}) c_\mu{}^* c_\nu \Big/ \sum_\mu c_\mu{}^* c_\mu. \tag{3}$$

The indices μ or ν are summed over all Slater determinants used in constructing $\Psi_{ij\ldots}$. The net increment of

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F, denoted by $f_{ij\cdots}$, is defined to be the difference between $\Delta F_{ij\cdots}$ and the sum of net increments of all orders less than n that have indices that are subsets of $ij\cdots$. As a consequence of these definitions, the exact mean value of F is expressed as a sum of all net increments up to order N. This provides a practicable method of calculation if the net increments of order greater than two or three are found to be negligible. Calculations on Be and Ne atoms indicate that this is true for net increments of the electronic energy.[6,7]

The present paper is concerned with the extension of these ideas to properties of the wave function, such as a scattering amplitude, that are not expressible as stationary-state mean values.

II. BETHE-GOLDSTONE EQUATIONS FOR SCATTERING

Because of the complexity of processes that can occur in scattering by a many-particle system (inelastic scattering, induced ionization) the present discussion will be limited to elastic scattering of a single external particle. Extension of the formalism to include more complex processes is straightforward.

Let the scattering atom be represented by a Hartree-Fock wave function Φ_0, Eq. (1). Then the zeroth-order approximation to a wave function that describes scattering of an external electron is

$$\Phi^k = \det\phi_1(1)\cdots\phi_N(N)\phi_k(N+1)\,, \tag{4}$$

where ϕ_k is a continuum solution of the Hartree-Fock equation

$$\mathcal{H}_0\phi_k = \epsilon_k\phi_k\,, \tag{5}$$

where $\mathcal{H}_0$ is the Hartree-Fock one-electron operator defined for state Φ_0.[8] Since ϕ_k is a continuum function, if it were normalized to make (ϕ_k,ϕ_k) equal unity, the electron density would vanish in any finite region. There is no self-consistent effect on the occupied bound-state orbitals ϕ_i, $i\leq N$. The function ϕ_k, for wave number k, determines a set of zeroth-order phase shifts $\delta_l(0)$. For consistency with earlier notation, the symbol "det" in Eq. (4) means $[(N+1)!]^{-1/2}$ times the antisymmetrizing operator.

The first-order Bethe-Goldstone equation with index i is equivalent to a variational calculation with a trial function of the form

$$\Psi_i = \Phi^k + \textstyle\sum_{ab}\Phi_i^{ab}c_i^{ab}. \tag{6}$$

The indices ab refer to members of a complete set of normalized orbitals that are orthogonal to all occupied orbitals ϕ_i of the atomic Hartree-Fock reference state Φ_0. The index k refers to an unnormalized continuum orbital of momentum k, orthogonal to the N occupied orbitals ϕ_i but not to the unoccupied orbitals ϕ_a. The variational equations for Ψ_i, discussed in more detail in Sec. III, below, are equivalent to the Bethe-Goldstone scattering equation discussed by Mittleman.[5] Since the function ϕ_k satisfies equations that differ from Eq. (5), it will in general have different phase shifts. For this reason the continuum function determined by Eq. (5) will be denoted by $\phi_k(0)$, and the continuum function determined variationally from Eq. (6) will be denoted by $\phi_k(i)$. Since this function is not normalized, Ψ_i itself is not normalized, but ϕ_k and the coefficients c_i^{ab} contain an arbitrary common numerical factor.

Corresponding to $\phi_k(0)$, there is a set of gross phase shifts $\Delta_l(0)$, which by definition are equal to the net phase shifts of order zero, $\delta_l(0)$. The modified phase shifts obtained from the ansatz of Eq. (6), through the function $\phi_k(i)$, will be referred to as gross phase shifts $\Delta_l(i)$. Then the net phase shifts are defined by

$$\delta_l(i) = \Delta_l(i) - \delta_l(0)\,, \tag{7}$$

in analogy to the definition of gross and net increments of stationary-state mean-value properties used previously.[1,2] The intuitive meaning of $\delta_l(i)$ is clear—it represents the change in phase shift at momentum k due to virtual polarization of the orbital i, neglecting any interaction with the polarization of other orbitals.

The extension to higher-order effects is obvious. The Bethe-Goldstone equation of order n, for a set of n indices $ij\cdots$, is equivalent to variational calculation with a trial function expressed as a linear combination of Φ^k, Φ_i^{ac}, Φ_j^{bc}, $\cdots$, Φ_{ij}^{abc}, $\cdots$, including all determinants with occupied orbital indices belonging to subsets of $ij\cdots$. The continuum function $\phi_k(ij\cdots)$ determines gross phase shifts $\Delta_l(ij\cdots)$. A net phase shift $\delta_l(ij\cdots)$ is defined as the difference between the gross phase shift and the sum of all net phase shifts of lower order with indices belonging to subsets of $ij\cdots$.

By definition, the sum of all net phase shifts up to order N is the exact phase shift if inelastic processes cannot occur. Obviously an inelastic process would require a trial wave function with more than one continuum function ϕ_k. The assumption that the normalized orbitals ϕ_i, ϕ_a form a complete set means that in principle a function like Φ_i^{ak}, representing a static correction to the Hartree-Fock approximation for the scattering atom, is already included in Eq. (6) and in its higher-order generalizations. In practice, it would be desirable to include such terms explicitly if they have a significant effect on the phase shifts. Since ϕ_k is not assumed to be orthogonal to the unoccupied orbitals, such terms can be included without changing the structure of the theory.

In Eq. (6), the orbitals ϕ_a and ϕ_b describe polarization of occupied orbital ϕ_i and distortion of the continuum function ϕ_k near the scattering atom. To describe these localized effects, it should be adequate to include orbitals ϕ_a from a discrete complete set of normalized functions that vanish at infinite distance from the atom. Then

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the asymptotic behavior of Ψ_i is entirely determined by the continuum function ϕ_k. The same remark is valid for Bethe-Goldstone functions of higher order.

III. COMPUTATIONAL METHOD

When core excitations are neglected, Mittleman has shown that his derivation leads to the Bethe-Goldstone equations.[5] This is easily seen to be equivalent to the use of Eq. (6) if the latter is written in the form

$$\Psi_i=\mathcal{A}\Phi_i(1,\cdots,N-1)\chi^{ik}(N,N+1),\tag{8}$$

where $\mathcal{A}$ is an antisymmetrizing operator, Φ_i is the $(N-1)$-particle Slater determinant obtained by removing ϕ_i from Φ_0, and χ^{ik} is a two-particle Slater determinant

$$\chi^{ik}=\det\{\phi_i(N)\phi_k(N+1)+\sum_{ab}\phi_a(N)\phi_b(N+1)c_i^{ab}\}.\tag{9}$$

The sign of $\mathcal{A}$ in Eq. (8) depends on the position of orbital ϕ_i, and $\mathcal{A}$ includes a normalizing factor. As written here, χ^{ik} is not a spin eigenfunction. The functions $\chi_\pm$ considered by Mittleman are the spatial factors of the singlet and triplet components, respectively, of χ^{ik}. In general, Eq. (6) is a mixture of spin eigenstates, which can easily be projected out by taking linear combinations of functions with different values of M_S for the atom and m_s for the external electron. For the sake of simplicity, this will not be done here, and Eq. (6), which describes scattering of a polarized electron (definite m_s) by a polarized atom (definite M_S), will be used.

With these remarks, the Bethe-Goldstone equations follow directly from the condition[5]

$$(\Phi_i,(H-E)\Psi_i)=0,\tag{10}$$

where this notation indicates integration over variable sets $1,\cdots,N-1$, leaving an integro-differential equation in the remaining two variable sets that determines $\chi^{ik}(N,N+1)$. This is equivalent to requiring that the functional derivative of $(\Psi_i,(H-E)\Psi_i)$, taken with respect to variations of χ^{ik}, should vanish.

When the explicit orbital expansion given by Eq. (6) is used, this variational condition implies two statements. First, the ordinary partial derivative of $(\Psi_i,(H-E)\Psi_i)$ with respect to each of the coefficients c_i^{ab} should vanish. Second, the functional derivative with respect to variations of the continuum function $\phi_k(i)$ should vanish, subject to the constraint that ϕ_k remain orthogonal to the occupied orbitals ϕ_i of reference state Φ_0. The first of these statements implies

$$(\Phi_i^{cd},(H-E)\Psi_i)=0,\quad c,d>N,\tag{11}$$

a set of inhomogeneous linear equations for the coefficients c_i^{ab}. The second statement leads to an integro-differential equation for $\phi_k(i)$,

$$\mathcal{H}_0\phi_k(i)+\sum_{ab}c_i^{ab}(i|R|a)\phi_b=(E-H_{00})\phi_k(i)+\sum_j\lambda_j\phi_j,\tag{12}$$

which differs from the continuum Hartree-Fock equation (5) by inclusion of a polarization term. The coefficients λ_j are Lagrange multipliers needed to make ϕ_k orthogonal to the orbitals ϕ_j, $j\leq N$. Here H_{00} is the Hartree-Fock energy of the scattering atom. The operator R is defined by the equation

$$(i|R|a)\phi_b=(i|Q|a)\phi_b-(i|Q|b)\phi_a,\tag{13}$$

where $\sum_{ij}Q(ij)$ is the two-particle operator in the Hamiltonian H. If the orbitals ϕ_j, $j\leq N$, are Hartree-Fock orbitals (eigenfunctions of $\mathcal{H}_0$), then Eq. (12) implies that

$$\lambda_j=\sum_{ab}c_i^{ab}(ij|R|ab).\tag{14}$$

Equations (11) and (12) must be solved simultaneously or iteratively.

In analogy to the variational principle of Hulthén,[9] the trial wave function Ψ_i can be required to satisfy the additional condition that the functional $(\Psi_i,(H-E)\Psi_i)$ should be equal to zero. Since Eqs. (11) are already imposed, this is equivalent to requiring that

$$(\Phi^k,(H-E)\Psi_i)=0.\tag{15}$$

When expressed in terms of matrix elements this becomes a formula that determines the parameter E,

$$E=H_{00}+\epsilon_k+(k|k)^{-1}\sum_{ab}(ik|R|ab)c_i^{ab}.\tag{16}$$

Here ϵ_k is the Hartree-Fock energy of the continuum orbital ($\frac{1}{2}k^2$ in atomic units), and R is the operator defined by Eq. (13). Equation (16) also follows from Eq. (12).

The last term in Eq. (16) represents a correction to the energy of the scattering atom. This is most easily seen by considering an orbital ϕ_k that vanishes at infinity, so that $(k|k)$ can be set equal to unity. Then this orbital could be taken to be one of the set ϕ_b, giving an energy correction

$$\Delta E_i=\sum_a(ik|R|ak)c_i^{ak},\tag{17}$$

identical with the formula for the first-order Bethe-Goldstone energy of a stationary state.[10] When ϕ_k does not vanish at infinity, it will have finite amplitude throughout an infinite volume, and the norm $(k|k)$ becomes infinite. The coefficients c_i^{ab} are finite under these conditions, and the individual integrals $(ik|R|ab)$ are finite. Hence the last term in Eq. (16) vanishes unless the sum $\sum_{ab}$ diverges. In practice, the complete set of normalized orbitals would be truncated, and the sum $\sum_{ab}$ would consist of a finite number of finite terms, thus precluding any finite energy shift ΔE_i. It is for this reason, to avoid an attempt to expand the unnormalizable function ϕ_k as a linear combination of normalized orbitals, that it would be desirable to include terms like Φ_i^{ak} in Eq. (6) if correlation corrections to the free scattering atom are important.

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IV. DISCUSSION

In this paper the proposal by Mittleman,[5] to use the two-particle Bethe-Goldstone equation to describe electron scattering by an alkali atom, has been extended to a general theory of one-particle scattering by a many-particle system. The definition of net phase shift increments of successively higher orders makes it possible through a hierarchy of n-particle Bethe-Goldstone equations to obtain phase shifts of arbitrary accuracy.

A similar method has been shown to be practicable for calculation of the correlation energy of light atoms.[6,7] In addition to the evaluation and manipulation of large numbers of matrix elements of the atomic Hamiltonian for normalized atomic orbitals, for which the methods, developed in stationary-state calculations should suffice, there are special problems arising from the nature of the continuum orbital ϕ_k in scattering theory. Coulombic integrals must be evaluated in which the charge densities contain oscillatory as well as exponentially decreasing functions. In using the method outlined in Sec. III, a continuum integro-differential equation, Eq. (12), must be solved. However, since this equation has the same formal structure as the Hartree-Fock equations, considerable experience in the necessary numerical methods is available.

A very useful test of the practicability of the proposed method would be calculations of the phase shifts for low-energy elastic scattering of electrons by He and Ne atoms. Excellent calculations on He [11] and Ne [12] have recently been published, and the present method should be tested by its ability to refine or to systematize such work.

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Measurement of the Lamb Shift in the $n=4$ Level of He^+: RF Spectroscopy Using Time-Resolved Optical Detection*

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A microwave measurement of the $4s_{1/2}$–$4p_{1/2}$ separation in He^+ has been obtained, using a method which involves time-resolved optical detection. Population changes induced by the microwaves in the $4s$ $(m=+\frac{1}{2})$ state are observed via intensity changes in the λ4686 Å $(n=4\rightarrow3)$ transition. The result of eleven measurements of the separation is $1766._0\pm7._5$ MHz. The lifetime of the $4s_{1/2}$ state was measured to be $(1.3_6\pm0.2_0)\times10^{-8}$ sec.

I. INTRODUCTION

THE fine structure of the $n=4$ level in He^+ has been the subject of several experimental investigations. Series[1] performed a high-resolution optical study of the λ4686 Å radiation ($n=4\rightarrow3$ transition in He^+) produced in a hollow-cathode discharge tube, and reported agreement with the theory except for a large shift of the $4^2P_{1/2}$ level downward from the predicted position.

A similar study by Herzberg[2] showed satisfactory agreement with the theory for all components of the λ4686 Å line.

Roesler and DeNoyer[3] investigated the helium hollow-cathode discharge and concluded that differential Doppler displacements of the spectral lines originating from the four $n=4$ levels could cause large shifts in the experimentally determined positions of the levels.

Roesler and Mack[4] studied the λ4686 Å radiation from a hollow-cathode discharge tube and reported over-all agreement between the experimentally determined positions of the components and the positions predicted by the theory, including quantum-electrodynamic corrections. The accuracy of these optical measurements was not sufficient to test the quantum electrodynamic theory to better than a few percent.

Lea, Leventhal, and Lamb[5] have reported the results of preliminary measurements on the $4^2S_{1/2}$–$4^2P_{1/2}$ and $4^2P_{3/2}$–$4^2P_{1/2}$ separations. Their method employs a dc electron beam to produce excited He^+ and a rf field to induce $4^2S_{1/2}$–$4^2P_{1/2}$ or $4^2P_{3/2}$–$4^2S_{1/2}$ transitions which are observed as intensity variations in the λ1215 Å ($n=4\rightarrow2$) radiation. Their result for the Lamb shift is 1765±20 MHz, which agrees with the theoretical value of 1769 MHz obtained from the work of Erickson.[6]

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