PHYSICAL REVIEW A VOLUME 7, NUMBER 1 JANUARY 1973

Application of Many-Body Green's Functions to the Scattering and Bound-State Properties of Helium*

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(Received 21 June 1972)

The approximation scheme suggested by Schneider, Taylor, and Yaris is applied to the scattering and the bound-state properties of the helium atom. Elastic scattering phase shifts for *s*, *p*, and *d* partial waves, ionization potentials, one-electron ground-state properties (i.e., electron densities, the natural orbitals, and the ground-state energy), and excitation energies from the ground to the excited states of helium have been calculated *simultaneously* from the linear-response function and one-particle Green's function. This simultaneity is made possible by concentrating all computational effort on calculating the one- and two-particle amplitudes rather than on the ground- and excited-state wave functions. These amplitudes can be directly related to almost all the properties of physical interest in atomic and molecular systems. Our results for both the scattering- and stationary-state properties are in good agreement with experiment and other previous calculations.

I. INTRODUCTION

In recent years there have been several attempts to exploit the Green's-function formalism, developed in quantum field theory, for calculating atomic and molecular properties.[1-12] The Green's-function formalism has substantial advantages over conventional wave-function methods.[11,12] The most important feature of this technique is that almost all physical properties can be expressed in terms of the one- and two-particle Green's functions (G_1 and G_2).[13] Thus, it is possible to calculate electron densities, density matrices,[4,5] transition amplitudes,[8] excitation energies, ionization potentials,[4,5] optical potentials,[2-5] and elastic[2,3] and inelastic scattering[11] cross sections directly without recourse to the actual computation of the correlated ground- and excited-state wave functions. Moreover, *all* of these can be calculated *simultaneously*. This can be a considerable savings in computational time and effort. In essence, what we have achieved computationally is to realize that in the calculation of the above-mentioned properties (working in a matrix or basis-set representation and choosing a basis set that is reasonable for the desired properties) the major part of the integrations and data handling can be done in common by obtaining G_1 and G_2. It has to be pointed out also that in this formalism the full many-body problem is reduced to a set of one- and two-body problems, albeit with nonlocal and energy-dependent effective potentials.[7,14] (These potentials account for the interaction of one and two particles, respectively, with the rest of the electrons.) Computationally this means that only one- and two-variable integrodifferential equations have to be solved.[5,14]

In this paper we apply the approximation scheme suggested by Schneider, Taylor, and Yaris,[7] called the generalized random-phase approximation (GRPA), to the scattering- and bound-state properties of the helium atom. This scheme is based on the Martin–Schwinger form[15] (using functional differentiation) of the Green's-function technique. One remarkable feature of the GRPA, as opposed to some of the earlier attempts to apply Green's-function theory to atomic physics, is that the polarization part of the optical potential is expressed in terms of a physically meaningful quantity, the generalized response function. The same scheme provides an equation for the generalized response function, which is identified as the random-phase approximation (RPA)[16] or time-dependent coupled Hartree–Fock (HF) approximation[17] for this quantity. The RPA has been used with considerable success by Dalgarno and others[18,19] to compute various frequency-dependent responses. This is a major conceptual advantage of being able to transfer an approximation known to be accurate for one physical property to the calculation of a seemingly unrelated quantity. In a complementary work,[20] the polarization part of the

GRPA optical potential has been analyzed and related to experimental quantities such as dynamical polarizabilities and shielding factors. It has been shown that it contains all dipole, quadrupole, nonadiabatic, orthogonality, and exchange terms in a compact and closed form.

In the GRPA, both the equations of motion for the response function and for the one-particle Green's function, within our approximation for the optical potential, are solved. There have been other calculations of the optical potential, which used the Brueckner–Goldstone perturbation approach and primarily aimed at computing scattering cross sections.[2,3] In all of these calculations, no attempt was made to diagonalize the effective one-particle Hamiltonian. In the present work, elastic scattering s-, p-, and d-wave phase shifts, ionization potentials, the ground-state energy, natural orbitals, and the excitation energies from the ground state to the excited states were calculated in a single computation.

On the basis of the numerical results we can conclude that the GRPA optical potential is capable of yielding one-particle properties to experimental accuracy and two-particle properties to 5–10% accuracy of the experiment. These results were not unexpected since our truncation procedure amounts to making an approximation to the three-particle Green's function. Since the two-particle Green's function is directly related to the three-particle Green's function G_3 through its equation of motion, it is significantly more sensitive to any approximations to G_3. It is possible to improve the present theory by examining higher-order effects. This has been done[21] and the results will appear in a future paper. From a computational point of view, more drastic approximation will have to be introduced into these higher-order equations to get a tractable theory. We do not expect these approximations to have any important adverse effects on any of our numerical results since we are interested in improving the present calculation by 5%. In addition, this higher-order theory is essential to obtain accurate inelastic differential scattering cross sections and resonances in the elastic scattering. However, there are properties like the average values of operators in excited states that are not easily obtainable in this theory.

In Sec. II, we present an outline of the GRPA.[7,11] No attempt is made to make this section complete. Instead, we outline the physics of the truncation procedure and summarize the important equations.

II. THEORY

We begin by considering the effect of an electron scattering from an atom or molecule. The simplest interaction is the electrostatic effect of the target electrons on the incoming electron. For low incoming electron energy, exchange and distortion effects also play important roles. The distortions are basically due to the polarization of the atomic charge cloud by the incident electron. One can then think of the incident electron as moving in the potential of the polarized target. Since the incident electron is moving, the target feels not only a static electric field in which the external electron moves but also that felt by the target electrons. Thus the external electron probes the interaction between target electrons as well as reacting to the distortions of the target density due to its own presence. The basic contribution of Ref. 7 was to show how the effects of *polarization* and *exchange* could be naturally incorporated into the Green's-function method of Martin and Schwinger.[15] In brief outline, the scheme involves the solution of two basic equations; the equation for the linear-response function of the target and the equation for the one-particle Green's function. The first of these equations, that for the linear-response function of the target, is identical with the equation of the random-phase approximation (time-dependent coupled Hartree–Fock theory).[16,17] The second equation, an integrodifferential equation for the Green's function, depends upon a knowledge of the target-response function. The dependence on the target response appears in the self-energy function or optical potential that governs the equation of motion for the Green's function. This optical potential is the true nonlocal energy-dependent potential seen by a particle moving in the field of the ground-state target. On the basis of the calculation of various frequency-dependent moments with the time-dependent HF method and from double-perturbation investigations, one can expect very accurate target polarizations. Having obtained the response function and optical potential, we now proceed to use that result to *solve* for the one-particle Green's function. In solving for the Green's function, one takes explicit account of the interaction of the polarized target and the incident electron and also adds further correlation effects to the target. The basic equations used in the calculation may be summarized as follows:

$$G(\vec{r}_1, \vec{r}_1', z) = \sum_{\alpha=1}^{N} \frac{\phi_\alpha(\vec{r}_1)\,\phi_\alpha^*(\vec{r}_1')}{z - E_\alpha - i\epsilon} + \sum_j \frac{\phi_j(\vec{r}_1)\,\phi_j^*(\vec{r}_1')}{z - E_j + i\epsilon} \tag{1}$$

$$= G^< + G^> \tag{1a}$$

and

$$R(\vec{r}_1 \vec{r}_2 \vec{r}_1' \vec{r}_2', z) = \sum_n \frac{\operatorname{sgn}(W_n)\, X^n(\vec{r}_1' \vec{r}_1)\, X^{n*}(\vec{r}_2 \vec{r}_2')}{W_n - z - i\epsilon \operatorname{sgn}(W_n)}\,, \tag{2}$$

where

$$X^n(\vec{r}_1\,\vec{r}_1') = \sum_{a,c} X^n_{ac}\,\phi^*_a(\vec{r}_1)\,\phi_c(\vec{r}_1') ,$$

α is the occupied orbital (hole), j is the unoccupied orbital (particle), a and c are either occupied or unoccupied orbitals, ϕ_α and ϕ_j are the Dyson amplitudes, X^n is the Bethe–Salpeter amplitude, E_k is the orbital energy of the electrons, W_n is the excitation energy from the ground to excited states of the system, and ϵ is an arbitrarily small positive number.

The equations satisfied by the Dyson amplitude and the Bethe–Salpeter amplitude can be written as follows[7]:

$$h_1(\vec{r}_1)\,\phi_n(\vec{r}_1) + \int d\vec{r}_1'\,\Sigma\,(\vec{r}_1\,\vec{r}_1', E_n)\,\phi_n(\vec{r}_1') = E_n\,\phi_n(\vec{r}_1) , \tag{3}$$

$$(E_c - E_a - W_n)\,X^n_{ac} = (N_c - N_a)\sum_{b,d}\,(V^{db}_{ac} - V^{ab}_{dc})\,X^n_{bd} , \tag{4}$$

where h_1 is the kinetic energy plus nuclear attraction, Σ is the optical potential, $V^{bd}_{ca} = \langle ad\,|\,1/r_{12}\,|\,cb\rangle$, $N_a = 1$ if $a \in G^<$ and is 0 otherwise, and indices a, b, c, and d represent both occupied and unoccupied orbitals,

$$\Sigma(\vec{r}_1\,\vec{r}_1', z) = \Sigma_{\mathrm{HF}}(\vec{r}_1\,\vec{r}_1') + \Sigma^<(\vec{r}_1\,\vec{r}_1', z) + \Sigma^>(\vec{r}_1\,\vec{r}_1', z) , \tag{5}$$

where Σ_{HF} is the Hartree–Fock potential,

$$\Sigma^<(\vec{r}_1\,\vec{r}_1', z) = \sum_{W_n<0}\;\sum_{\alpha\in G^<}\;\sum_{abcd} \frac{V_{bd}(\vec{r}_1)\,X^n_{ca}\,X^{n*}_{db}}{z - E_\alpha - W_n - i\epsilon} \times [V_{ac}(\vec{r}_1')\,\phi_\alpha(\vec{r}_1)\,\phi^*_\alpha(\vec{r}_1') - V_{\alpha c}(\vec{r}_1')\,\phi_\alpha(\vec{r}_1)\,\phi^*_a(\vec{r}_1')] ,$$

$$\Sigma^>(\vec{r}_1\,\vec{r}_1', z) = \sum_{W_n>0}\;\sum_{j\in G^>}\;\sum_{abcd} \frac{V_{bd}(\vec{r}_1)\,X^n_{ca}\,X^{n*}_{db}}{z - E_j - W_n + i\epsilon} \times [V_{ac}(\vec{r}_1')\,\phi_\alpha(\vec{r}_1)\,\phi^*_\alpha(\vec{r}_1') - V_{\alpha c}(\vec{r}_1')\,\phi_\alpha(\vec{r}_1)\,\phi^*_a(\vec{r}_1')] ,$$

$$V_{ab}(\vec{r}_x) = \int d\vec{r}_y\,\phi^*_a(\vec{r}_y)\,\frac{1}{r_{xy}}\,\phi_b(\vec{r}_y) .$$

Both $\Sigma^<$ and $\Sigma^>$ include direct and exchange polarization potentials.

These equations are written in the forms that are most suitable for computation. From a simple examination of these equations, we see the possibility of extracting ionization potentials and excitation energies directly and not as the difference of two total energies. The continuous spectrum of Eq. (3) provides us with elastic scattering phase shifts. The Bethe–Salpeter amplitude can be simply related to the generalized oscillator strength.[8] The one-particle density matrix[4] (and therefore natural orbitals) can be extracted from the Green's function by an appropriate contour integration. The total ground-state energy can also be computed from the one-particle Green's function by a contour integration. In summary, we see how a knowledge of the one-particle Green's function and the linear-response function provides a host of static and dynamical information about the system under study. These properties are extracted from the Green's function and linear response in *one* calculation and without recourse to the correlated ground- and excited-state wave functions.

III. NUMERICAL PROCEDURE

The calculation of the e^--He elastic scattering phase shifts and bound-state properties of He was carried out in five basic steps.

(i) Step one was to solve the Hartree–Fock equation for He on a finite basis set of Slater orbitals.[22] The basis set used consisted of 36 radial functions (12 s-type, 12 p-type, and 12 d-type). This step provides us with the Hartree–Fock Green's function in diagonal matrix form and all necessary integrals to perform the subsequent steps in the computation.

(ii) The second step was to solve the RPA eigenvalue problem,[16] given in Eq. (4), using the Hartree–Fock Green's function obtained from step 1. The RPA eigenvalues are the excitation energies of He. The eigenvalues and eigenfunctions (generalized oscillator strengths) are then used to construct the optical potential.

(iii) The third step was to combine the results of steps one and two into the optical potential of Eq. (5). The optical potential is then subjected to a partial-wave analysis in order to simplify subsequent calculations. Since the long-range nature of the Hartree potential must be reproduced accurately in the calculation of the phase shifts, we have tabulated this potential numerically. The exchange and polarization parts of the optical potential were evaluated using the basis-set expansion described in step one. In the calculation of the stationary properties of the helium atom it is not necessary to reproduce the Hartree potential exactly and the entire calculation is done with the basis given above. In this calculation, the imaginary part of Σ is neglected (Σ is real below the first inelastic threshold).

(iv) The fourth step was to solve the Dyson equation [Eq. (3)], which is now a one-dimensional integrodifferential equation for the partial-wave phase shifts, using the optical potential from step three. This equation is converted to an integral equation using the "free-wave" Green's function and integrated numerically using the noniterative technique of Sams and Kouri.[23] The numerical integrations were done using Simpson's rule quadrature formula. The region of integration was divided into ten zones with the integration mesh size doubling in each zone. The initial mesh size was chosen to be 0.01 a.u. As a check on the method, the phase shifts were calculated using only the Hartree–Fock potential. The results were in good agreement with previous static-exchange calculations found in the literature.[3] The calculations were performed with smaller basis sets and different orbital exponents to ensure that the set expansion has converged with respect to the calculated properties.

(v) The last step was to solve the Dyson equation with the optical potential of step 3 for the ionization potential, ground-state energy, and natural orbitals.[4,5] These quantities were evaluated by finding the poles and residues of the Green's function in the region of negative energy. The determination of the poles of the Green's function involves guessing an energy, evaluating the optical potential at that energy, and diagonalizing the Dyson equation in matrix form. This procedure is iterated until input and output energies agree to eight decimal places.

The final form[14] for the one-particle Green's function can be written in spectral form as

$$G(\vec{r}_1\,\vec{r}_1{}', z) = \sum_n \frac{g_n^{-1}\,\phi_n(\vec{r}_1)\,\phi_n^*(\vec{r}_1{}')}{z - E_n}\,, \tag{6}$$

where

$$g_n = 1 - \frac{dE_n(z)}{dz}\bigg|_{z=E_n}\,.$$

The one-particle density matrix[4,5] can be obtained by integrating $G^<(\vec{r}_1, \vec{r}_2, z)$ in the upper half of the complex z plane. In the spectral representation this amounts to "pole picking":

$$\gamma(\vec{r}_1\,\vec{r}_1{}') = \frac{1}{2\pi i}\oint_{\cap} G(\vec{r}_1\,\vec{r}_1{}', z)\,dz$$

$$= \sum_{E_n<0} g_n^{-1}\,\phi_n(\vec{r}_1)\,\phi_n^*(\vec{r}_1{}')\,. \tag{7}$$

TABLE I. Comparison of several theoretical calculations of s-Wave phase shifts for e^--He elastic scattering.

Energy (eV)	Phase shifts (in radians) Present results	Ref. 27	Ref. 25	Ref. 3	Ref. 26
0.136	3.0367	3.017			
0.50	2.8898	2.8945	2.8997		
1.00	2.7813	2.7869			
2.00	2.6304	2.6371			
2.50	2.5669	2.5783			
3.40	2.4741	2.4878	2.4942	2.4781	
5.00	2.3471	2.3590			
7.65	2.1797	2.1979	2.2012		
10.00	2.0699	2.0877			
13.605	1.9372	1.955	1.9530	1.9412	1.9330
21.25	1.7403	1.756	1.7483		

TABLE II. Comparison of several theoretical calculations of p-wave phase shifts for e^--He elastic scattering.

Energy (eV)	Phase shifts (in radians) Present results	Ref. 27	Ref. 25	Ref. 3	Ref. 26
0.136	0.0094	0.00306			
0.50	0.0175	0.0118	0.0128		
1.00	0.0226	0.0242			
2.00	0.0506	0.0497			
2.50	0.0606	0.0625			
3.40	0.0806	0.0845	0.0926	0.0732	0.0750
5.00	0.1189	0.1213			
7.65	0.1684	0.1729	0.1891		
10.00	0.2079	0.2094			
13.605	0.2510	0.2508	0.2749	0.2449	0.2477
21.25	0.3133	0.3014	0.3332		

Since the $\{\phi_n\}$ do not form an orthonormal set, we must diagonalize $\gamma(\vec{r}_1\,\vec{r}_1{}')$ in our original Hartree–Fock basis. This yields the natural orbitals and occupation numbers directly in terms of the occupied and virtual Hartree–Fock functions. The ground-state energy[4,5] can also be evaluated by integrating the Green's function in the upper half-plane via

$$E_{\mathrm{GS}}^{\mathrm{tot}} = -\frac{i}{4\pi}\oint_{\cap} dz \lim_{\vec{r}_1{}'\to\vec{r}_1}\int d\vec{r}_1\,(z + h_1(\vec{r}_1))\,G(\vec{r}_1\,\vec{r}_1{}', z)\,, \tag{8}$$

where

$$h_1(\vec{r}) = -\tfrac{1}{2}\nabla^2 - Z/r\,.$$

All diagonalizations in this calculation were performed using the "QR algorithm."[24] The entire calculation takes 30 min on the IBM-360-75.

IV. RESULTS AND DISCUSSION

A. Elastic Scattering Phase Shifts

The phase shifts from this calculation for s, p, and d waves in the energy range 0.136–21.25 eV are presented in Tables I, II, and III, respectively. These phase shifts are compared with those obtained from the theoretical calculations of Pu and Chang,[3] Duxler *et al.*,[25] Knowles and McDowell,[26] and Callaway *et al.*[27] For a visual comparison, all these calculations and the theoretical fit to the experimental data by Bransden, Knowles, and McDowell[28] are plotted as a function of energy in Figs. 1–3. Our calculation of the d-wave phase shift should not be expected to be as accurate as our s- and p-wave phase shifts for the following reason: We chose to ignore orbitals of f and higher angular momentum in the construction of our optical potential. This introduces an asymmetry in our cal-

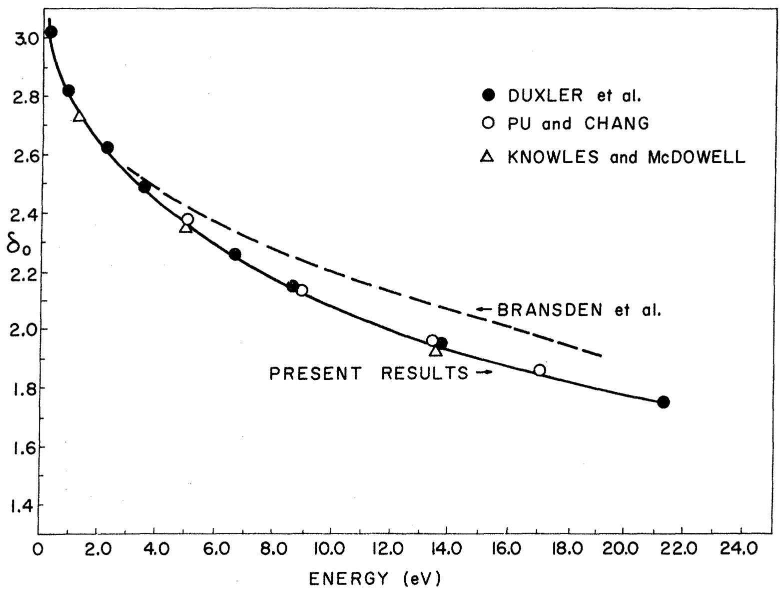

FIG. 1. e^--He s-wave phase shifts.

culation for d waves when compared to our s- and p-wave phase shifts.[29] In addition, we think that our d-wave basis is not large enough to represent all those parts of the optical potential important to the d-wave phase shifts.

A few comments on the previous theoretical calculations are in order. Pu and Chang[3] used many-body perturbation theory to construct an energy-dependent optical potential but neglected the terms in $\Sigma^<$ depending on the bound part of one-particle Green's function (i.e., $G^<$) and used the distorted-wave Born approximation to compute the phase shifts. Quite recently Knowles and McDowell[26] have extended the calculation of Pu and Chang by including the exclusion principle violating (EPV) diagrams and higher partial waves. They too use the distorted-wave Born approximation to calculate the phase shifts. Callaway *et al.*[27] have included contributions from certain direct nonadiabatic terms in the potential but have neglected the exchange-polarization terms completely. The full polarized-orbital method of Temkin[30] has recently been applied to the e^--He problem by Duxler *et al.*[25] This technique includes all adiabatic effects in the scattering but ignores the energy dependence of the optical potential completely.

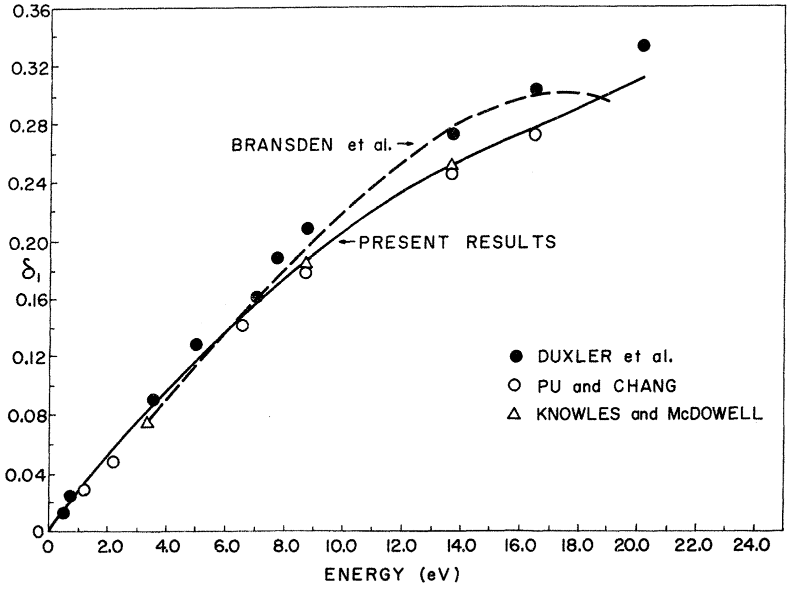

FIG. 2. e^--He p-wave phase shifts. The turnover in the results of Brandsen *et al.* (Ref. 28) around 16 eV is possibly not realistic (see Sec. IV A).

TABLE III. Comparison of several theoretical calculations of d-wave phase shifts for e^--He elastic scattering.

Energy (eV)	Phase shifts (in radians) Present results	Ref. 27	Ref. 25	Ref. 26
1.00	0.002 636	0.0029		
2.00	0.003 905	0.0060		
2.50	0.005 217	0.0076		
3.40	0.005 332	0.0104	0.0115	0.007 45
5.00	0.008 687	0.0154		
7.65	0.013 675	0.0239	0.0262	
10.00	0.019 241	0.0312		
13.605	0.028 19	0.0419	0.0458	0.035 16
21.25	0.047 98	0.0620	0.0676	

The present calculation includes (i) direct and exchange polarization on an equal basis, (ii) all nonadiabatic effects, and (iii) EPV terms and solves the Dyson equation exactly for the phase shifts. This should exhaust all the important physical effects for low-energy e^--He elastic scattering.

An examination of Figs. 1–3 reveals that for almost all incident energies the theoretical calculations are below the experimental curves. The close agreement of our calculation with the recent results of Knowles and McDowell[26] suggests that the semiempirical analysis of Bransden, Knowles, and McDowell[28] might slightly overestimate the phase shifts. Both our calculation and that of Knowles and McDowell[26] account for all important effects in the optical potential. It is highly unlikely that a more sophisticated treatment would cause the calculated phase shifts to increase to any significant degree.

TABLE IV. Ionization potential (IP) and Ground-state energy (GSE) of helium atom (including s, p, and d symmetries).

	Hartree—Fock (a.u.)	Exact (a.u.)	Present results (a.u.)	Ref. 4 (a.u.)
IP	−0.9175	−0.9037 (Ref. 38)	−0.9033	−0.906
GSE	−2.8617	−2.903 72 (Ref. 39)	−2.9056	−2.9009

This calculation can also be extended to arbitrarily high incident energies (for example, $E = 500$ eV), as demonstrated by LaBahn and Callaway[31] and Khare and Shobha,[32] because it includes nonadiabatic polarization effects in a rigorous manner.[20] However, it has to be pointed out that the resonances in the e^--He elastic scattering[33] (for example, the well-known 19.3-eV ^2S resonance) cannot be calculated in the present scheme. The inclusion of resonances in this method requires a coupling of the triplet part of the response function to the one-particle Green's function in the optical potential. Since the optical potential used here contains only the singlet part of the response function, a high-order truncation scheme is needed to treat resonances in the Green's-function formalism. This truncation must bring in the particle-particle interactions that are omitted in the RPA approximation.

B. Ionization Potential, Ground-State Energy, and Natural Orbitals

The ionization potential and ground-state energy of the He atom are presented in Table IV and are compared with experiment and the Green's-function calculation of Reinhardt and Doll.[4,5] The

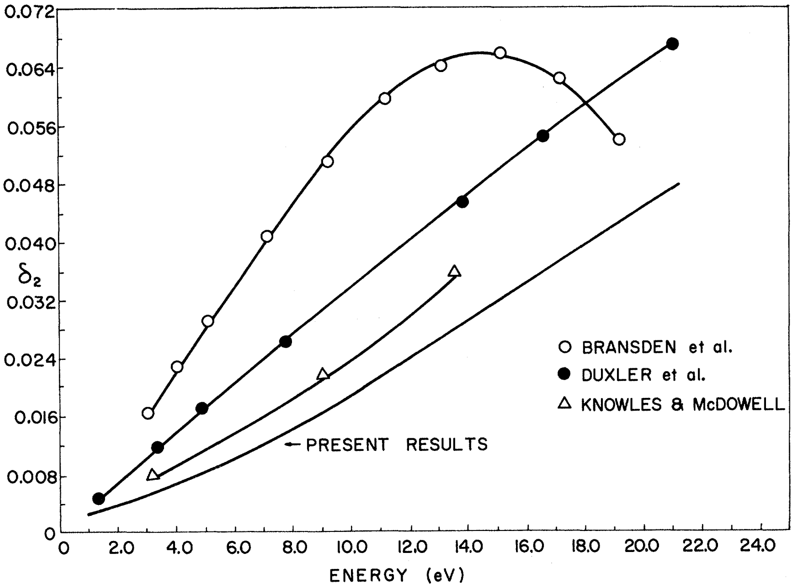

FIG. 3. e^--He d-wave shifts. The turnover in the results of Brandsen *et al.* (Ref. 28) around 14 eV is possibly not realistic (see Sec. IV A).

TABLE V. Occupation numbers of natural orbitals of helium atom.

		Present results		Ref. 34		Ref. 4		Ref. 35[a]	
Type	k	n_k	Total	n_k	Total	n_k	Total	n_k	Total
s	1	0.993 193		0.991 863		0.994 612		0.992 148	
	2	0.002 559		0.003 849		0.002 333		0.004 053	
	3	0.000 089		0.000 054		0.000 068		0.003 665	
	4	0.000 008		0.000 005		0.000 004			
	5	0.000 001				6×10^{-9}			
	6–12	$<10^{-6}$	0.995 850		0.995 771		0.996 017		0.999 866
p	1	0.003 7465		0.003 896		0.002 690		0.001 302	
	2	0.000 2129		0.000 136		0.000 143		0.000 031	
	3	0.000 0223		0.000 004		0.000 011			
	4	0.000 0035				5×10^{-7}			
	5	0.000 0007							
	6–12	$<10^{-7}$	0.003 986		0.004 036		0.002 844		0.001 333
d	1	0.000 2788		0.000 180		0.000 207		0.000 029	0.000 029
	2	0.000 0362		0.000 004		0.000 018			
	3	0.000 0060				2×10^{-7}			
	4	0.000 0013					0.000 225		
	5	0.000 0004							
	6–12	$<10^{-7}$	0.000 324		0.000 184				
Sum			1.000 150		0.999 991[b]		1.000 086		1.001 228

[a] In this paper a configuration-interaction-type wave function for helium atom is given in terms of natural orbitals. The results quoted here correspond to the square of the expansion coefficients of their function ψ_2, which includes (s, p, d) natural orbitals.

[b] These authors include f-type symmetry also in their calculation. With f contribution added to this result, the trace is exactly equal to 1.0. They calculate the one-particle density matrix by the method of superposition of configurations. The density matrix was then diagonalized to get natural orbitals.

agreement between theory and experiment for the ionization potential is superb. Our value for the correlation energy is 4.5% above the experimental value. Since there is no minimum principle for the energy when expressed as a functional of the one-particle Green's function, it is possible to overestimate the correlation energy. In spite of this, we regard our results for the total ground-state energy as meaningful for the following reason: The one-particle Green's function has been used to compute phase shifts, ionization potentials, and natural orbitals, all to a high degree of accuracy. It is highly unlikely that these properties, which depend on quite similar physical effects, would be given so well by our truncation scheme and not also the ground-state energy. Another check on the calculation is to compute the trace of the Green's function. This trace, which should be equal to the number of electrons in the system, is shown in Table V. This result verifies that we have conserved particles in our approximate self-energy. The natural orbitals[34] are obtained by diagonalizing the density matrix in the Hartree–Fock basis after performing the contour integration of Eq. (8). The results are presented in Table V and compared with other theoretical calculations.[4,5,34,35] The very small lack of trace conservation is not due to numerical errors but arises from using an approximation to the exact optical potential. From our one-particle density matrix it is possible to calculate a variety of physical properties to a high degree of accuracy.

TABLE VI. Low-lying singlet excitation energies of helium atom.

Excitation	Exact (Refs. 38 and 40) (a.u.)	Present results (a.u.)	Ref. 37 (a.u.)	Ref. 19 (a.u.)
$1\,^1S\rightarrow 2\,^1S$	0.7577	0.7756		
$1\,^1S\rightarrow 3\,^1S$	0.842	0.8754		
$1\,^1S\rightarrow 2\,^1P$	0.779 88	0.7970	0.7965	0.796 97
$1\,^1S\rightarrow 3\,^1P$	0.848 58	0.874 98	0.8637	0.8636
$1\,^1S\rightarrow 4\,^1P$	0.872 65	0.9794[a]	0.9083	0.887 21
$1\,^1S\rightarrow 5\,^1P$	0.8842	1.1897[a]		0.898 21
$1\,^1S\rightarrow 3\,^1D$		0.8648		
$1\,^1S\rightarrow 4\,^1D$		0.925 29[a]		

[a] These excitation energies are greater than the ionization limit. This is caused by the use of finite set of HF orbitals (occupied and virtual orbitals). This discrepancy can be easily removed by solving the RPA eigenvalue problem numerically as in column 5. These remarks are also valid for optically forbidden transitions (see Sec. IV C).

C. Excitation Energies and Oscillator Strengths

The eigenvalues and eigenvectors of the RPA equation represent excitation energies[16] and generalized oscillator strengths,[8,36] respectively. The low-ly-

TABLE VII. Low-lying triplet excitation energies of helium atom.

Excitation	Present results[a]	Exact (Refs. 38 and 40)
$1\,^1S \rightarrow 2\,^3S$	0.7236	0.728 41
$1\,^1S \rightarrow 3\,^3S$	0.8541	0.834 98
$1\,^1S \rightarrow 2\,^3P$	0.7733	0.7703
$1\,^1S \rightarrow 3\,^3P$	0.8632	
$1\,^1S \rightarrow 3\,^3D$	0.8647	

[a] See Sec. IV C regarding high-lying excitation energies.

ing singlet and triplet excitation energies of helium atom are presented in Table VI and VII. In the case of the optically allowed singlet transition we can compare our results with the variational solutions of the coupled Hartree–Fock equations of Sengupta and Mukherji[37] and the accurate numerical solutions of the same equations by Jamieson.[19] This comparison immediately shows that the RPA equation is capable of predicting accurate excitation energies for both low- and high-lying atomic transitions. Unfortunately, it is difficult for variational calculations to reproduce the proper functional form of the high-lying states without resorting to extremely large basis sets. This is particularly true of variational solutions that, like ours, are based on Hartree–Fock virtual orbitals that all lie in the continuum. However, if one solves the RPA equations numerically, one predicts the excitation energies[19] and oscillator strengths[8] to an accuracy of about 5%. It should be emphasized that we could have calculated these properties from our solution to the RPA eigenvalue problem but did not do so since they were already available. We have sacrificed accuracy in these properties in order to simplify the computation of properties that depend upon the one-particle Green's function. This has no effect on our phase shifts since only the average behavior of the response function is needed for the construction of the optical potential.

This theory should, in principle, be judged on our G_1 properties and RPA quantities of Schneider[8] and Jamieson,[19] since these results exhibit the full power of the method.

ACKNOWLEDGMENTS

We thank Dr. R. K. Nesbet and the IBM Corporation for supplying us with a copy of his CON360 programs, which enabled us to solve the Hartree–Fock eigenvalue equations. One of us (B. S. Y.) greatly appreciates the help of Lowell Thomas in the use of CON360. We also thank Professor M. R. C. McDowell and Dr. R. K. Nesbet for supplying us the results of their phase-shift calculations prior to publication. We are grateful to Professor K. Ruedenberg for criticizing and improving our manuscript.

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*Work partially supported by the National Science Foundation under Grant Nos. 53-4815-2095, GP-7861, and GP9549 and partially by the Petroleum Research Fund of the American Chemical Society under Grant No. PRF 4341-AC5.

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These authors calculated s-, p-, d-, and f-wave e^- – He elastic scattering phase shifts by the variational method. Their results for d-wave phase shifts were obtained *with* and *without* the inclusion of f orbitals in the basis set. Our results for d-wave phase shift are in very good agreement with their d-wave results with s, p, and d basis.

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PHYSICAL REVIEW A VOLUME 7, NUMBER 1 JANUARY 1973

Scattering of Light Ions in the Weakly Screened Coulomb Field of Gold Nuclei

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(Received 10 July 1972)

The differential cross section for scattering of 300–2000-keV H^+ and 300–500-keV He^+ and Li^+ through 3°–15° by gold targets has been measured. The targets were thin (34–220 $\mu g/cm^2$), vacuum-deposited polycrystalline foils. To eliminate the influence of multiple scattering, several target thicknesses were used to allow extrapolations to zero thickness. The agreement between our experimental data, theoretical predictions, and published experimental data is found to be satisfactory.

I. INTRODUCTION

Elastic scattering of ions on atoms yields information on the screening of the Coulomb interaction by the electrons surrounding the partners in the collision and is thus of interest for theoreticians as well as for experimentalists. While it is fairly straightforward to calculate the electron distribution of a single atom from a statistical model,[1] the description of the electron distribution of two colliding atoms is more complicated. For close collisions, interaction by an exponentially screened Coulomb potential[2] is found to work rather well, but this interaction potential falls off much too rapidly with distance. A Thomas–Fermi (TF) calculation may then be attempted also for the two-atom case.

In a comprehensive paper, Lindhard *et al.*[3] showed that the similarity properties of atoms in the TF model, together with some simple assumptions, allowed a very simplified expression for the differential cross section. They expressed the cross section as being a function of one single parameter proportional to the product of projectile energy and recoil energy in the collision. If, further, these energies are expressed in dimensionless TF energy units, it is necessary to calculate only a single universal function numerically. By means of a simple procedure, this function may then be used to find differential cross sections for all combinations of projectiles, targets, projectile energies, and scattering angles.

The experimental verification of the above-mentioned predictions has not been very extensive. Loftager *et al.*[4] investigated mainly the region of larger impact parameters corresponding to scattering in strongly screened fields. Other investigators[5,6] obtained a large number of experimental data that may be directly compared to those of the present paper, but these data were not analyzed to test the scaling properties, nor were they compared in absolute magnitude with the TF cross section.

Thus, there appears to be a need to investigate experimentally the results of Lindhard *et al.*[3], not only for the intrinsic interest in interaction potentials, but also because the weakly screened cross sections are important for further progress, for example, in the calculation of phenomena involving recoil energies of target atoms. Recent examples are calculations of sputtering yields[7] and radiation damage.[8]

The present experiments have been made partly for the above-mentioned purposes, partly for the purpose of examining the possibilities of using solid targets for measurements of scattering cross sections at relatively large impact parameters (see also Ref. 5). 300–2000-keV H^+ and 300–500-keV He^+ and Li^+ ions scattered through 3°–15° in the laboratory system were used. The targets