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Ab initio calculation of static atomic dipole polarizabilities

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The simultaneous optimization of the bound and continuum multiconfiguration Hartree-Fock orbitals for an electron scattered by an atom leads to a set of bound orbitals for the target atom that completely takes into account the polarization of the target by the electron. The polarized orbitals that are generated for zero kinetic energy and angular momentum of the continuum electron form an excellent basis for the calculation of the static dipole polarizability. We have done this for the ground states of the inert-gas atoms helium, neon, and argon. Our results agree extremely well with experimental measurements, indicating that this *ab initio* approach provides very good wave functions with which to determine highly accurate values of the polarizability.

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I. INTRODUCTION

The dipole polarizability, the quantity that describes the response of an atom or molecule to an external field, is a fundamental property of the atomic or molecular system. Its correct calculation can serve as a test of the wave functions that must describe the system in the presence of the field. Perhaps in no case is this more strongly felt than in the area of electron-atom or electron-molecule scattering.

It is well known that a basic problem in low-energy electron-atom scattering is how to represent the long-range polarization potential between the electron and the polarizable target, especially when a considerable portion of the polarizability derives from the continuum. Temkin [1] accounted for this effect by taking the view that the process could be represented as scattering of the electron by an atom which had been polarized by the incident electron. His approach led to the definition of a set of polarized orbitals which describe the atom in the presence of the incident electron. This polarized-orbital method was successfully applied to the scattering of electrons off hydrogen by Temkin and Lamkin [2] and has been used for a number of other systems as well [3–6].

Damburg and Karule [7] suggested a solution to this problem for electron-hydrogen scattering through the definition of a polarized pseudostate which could be included in the close-coupling approximation. Burke, Gallaher, and Geltman [8] used this pseudostate approach, with the pseudostate obtained from a first order perturbation calculation describing the static dipole distortion of the target in the field of a distant outer charge, with a substantial improvement over the usual close-coupling method.

Feautrier, Van Regemorter, and Lan [9] extended the polarized-orbital method of Temkin to coupled channels to obtain the appropriate polarized pseudostates. Lan, Le Dourneuf, and Burke [10] developed a general method for calculating any polarized pseudostate for a complex atom within a superposition of configurations framework. Lan [11] discussed the principle of constructing such pseudostates in a single configuration scheme based on the numerical solution of the first-order perturbation equation. Burke and Mitchell [12] made a first attempt at calculating multiconfigurational pseudostates and obtained the polarized pseudostates as linear combinations of configurations. They obtained results for helium, neon, argon, and nitrogen. Lan, LeDourneuf, and Burke [10], using their general method, obtained the polarized pseudostate and calculated atomic dipole polarizabilities for complex atoms such as C, N, and O. Miller and Kelly [13] used many-body perturbation theory to calculate the dipole polarizability of the neutral carbon atom in the $3p$ ground state. Billingsley and Krauss [14] and Stevens and Billingsley [15] calculated static dipole polarizabilities of atoms within a multiconfiguration self-consistent-field framework. Their method involves the direct solution of the multiconfiguration self-consistent-field equations of an atom in the presence of a perturbing field which is simulated by a charged particle. Robb [16] calculated the dynamic dipole polarizability of the ground state of beryllium and carbon atoms using an expansion of the perturbed-atomic-state wave function in terms of R-matrix states. Robb [17] also calculated the frequency-dependent dipole polarizability of the ground state of atomic nitrogen using the R-matrix method. Burke and Robb [18] developed a theory of electron scattering by complex atoms based upon the R-matrix method to calculate the static atomic dipole polarizabilities.

In recent years Saha has applied an expanded multiconfigurational Hartree-Fock (MCHF) technique [19] to the calculation of elastic electron-atom scattering cross sections [20–23]. The results for the total cross section at very low energy have been extremely good. This technique relies on a simultaneous optimization of both the bound and the continuum orbitals for each energy of the scattering electron. In this way the dynamic core-polarization effects can be very accurately taken into account *ab initio*. In the limit in which the kinetic energy and angular momentum of the scattering electron are equal to zero, the bound target orbitals which are generated should contain all the information about the static polarizability governing the response of the target to the external field of the electron. Thus, they form an ideal basis for the calculation of the atomic polarizability.

In the work which follows we describe a calculation of the static dipole polarizability based on the expansion of the distorted wave function in terms of the excited configuration states used to describe electron-atom scattering as discussed above. The polarized orbitals are first generated by application of the multiconfiguration self-consistent-field method to the electron-target system with minimization and determination of the bound orbitals for zero kinetic energy and angular momentum of the electron. These orbitals are then used in the traditional manner to perform the calculation of the static polarizability. As a test of the validity of this approach we have obtained results for the polarizability of the rare gases helium, neon, and argon.

II. THEORY

A. Dipole polarizabilities

The static dipole polarizability of an atomic system is defined through the expression

$$\alpha_\mu = 2\sum_k \int dk \frac{|\langle \phi_0 | M_1^\mu | \phi_k \rangle|^2}{E_k - E_0} . \tag{1}$$

(Atomic units are used throughout.) The summation and integration extend over all states ϕ_k, including the continuum, which are coupled to the initial state ϕ_0 by the dipole operator

$$M_1^\mu = \left[\frac{4\pi}{3}\right]^{1/2} \sum_{i=1}^{N} r_i Y_1^\mu(\hat{\mathbf{r}}_i) , \tag{2}$$

where N is the number of atomic electrons. For an atom in the gas phase it is sufficient to take $\mu = 0$, then $M_i^0 = \Sigma_i z_i$. Following Dalgarno and Davison [24], the expression for α given in Eq. (1) can be shown to be equivalent to the expression

$$\alpha = 2\sum_p \frac{|\langle \phi_0 | M_1^0 | \phi_p \rangle|^2}{E_p - E_0} , \tag{3}$$

where the polarized orbitals ϕ_p are solutions to the atomic Hamiltonian in the presence of the external field. Our approach is to determine these polarized orbitals through the MCHF method by selecting those bound states which are solutions to the full Hamiltonian, with scattering electron, for zero electron energy and angular momentum.

B. Polarized orbitals

As in earlier work, the distorted wave function for the scattering states is expanded in terms of members of a complete set of bound and continuum orbitals, as

$$\Psi(\gamma LS;N+1) = \sum_{j=1}^{m_t} a_j \Phi(\gamma_j L_t S_t;N)\phi_{kl} + \sum_{i=1}^{m} c_i \Phi(\gamma_i LS;N+1) , \tag{4}$$

where $\Phi(\gamma_j L_t S_t;N)$ are target wave functions coupling with the wave function of the scattered electron to form an eigenstate of L and the total spin angular momentum S. $\Phi(\gamma_i LS;N+1)$ are $(N+1)$-electron wave functions formed from bound orbitals and are included for polarization. The method of constructing the polarized orbitals for $l=0$ and $k^2=0$ involves the solution of coupled integrodifferential equations of the form

$$\left[\frac{d^2}{dr^2} + \frac{2z}{r} - \frac{l(l+1)}{r^2}\right] P_i(r) = \frac{2}{r}[Y_i(r)P_i(r) + X_i(r) + I_i(r)] + \sum_{i} \varepsilon_{ii'} P_{i'}(r) \tag{5}$$

by an iterative method as described in detail earlier [20]. The bound wave functions satisfy the boundary conditions

$$\lim_{r\to 0} P_i(r) = r^{l+1}, \quad \lim_{r\to\infty} P_i(r) = 0 \tag{6}$$

and the radial function for the scattering orbital for $l=0$ and $k^2=0$ satisfy the boundary conditions

$$\lim_{r\to 0} P_i(r) = r^{l+1}, \quad \lim_{r\to\infty} P_i(r) = A'(r-a) , \tag{7}$$

where a is the scattering length.

As the polarization of the target atoms by the scattering electron is very strong at zero energy, all the configurations which account for the polarization are considered in the expansion of the scattering function. The dipole polarization is taken into account by adding configurations generated by the replacement of the target orbitals with excited orbitals which reproduce dipole effects. The resulting set of coupled second-order integrodifferential equations, which can become quite large, is solved numerically by an iterative method which varies both the bound and the continuum orbitals simultaneously. Part of the output of this technique is the set of polarized orbitals ϕ_p which are then used to calculate α according to Eq. (3). The energy E_p is obtained by a direct evaluation of the N-electron atomic Hamiltonian in the state described by the polarized orbital. No further minimization is employed. We stress the fact that the polarized orbitals generated through this procedure contain all the necessary information about the polarization due to the external field.

III. RESULTS

To test our approach, we select inert-gas atoms because of two reasons. First, a number of theoretical and experimental results are available for these atoms, and we can compare our results with them. Second, inert-gas atoms have a closed shell in the ground state. Their configuration can only form a single LS state, ${}^1S_0$ in the

TABLE I. Contributions from the polarized orbitals to the static dipole polarizability of helium.

Initial state	Polarized orbital	ΔE_p (a.u.)[a]	Dipole matrix element	Contribution to α (a_0^3)	Total α (a_0^3)
HF	$2p$	0.859 58	1.078 51	0.902	
	$3p$	0.968 90	0.748 51	0.386	1.506
	$4p$	1.964 71	0.801 33	0.218	
	$2p$	0.900 31	1.053 46	0.822	
MCHF	$3p$	1.009 62	0.734 35	0.356	1.374
	$4p$	2.005 43	0.768 30	0.196	

[a]Energy difference $E_p - E_0$ from Eq. (3).

Russell-Saunders description. There are no unoccupied orbitals close enough in energy to the ground state to make a significant contribution to the polarizability. Thus, the polarizability becomes very sensitive to the distortion of the occupied orbitals. While it is easier to determine the polarizability for open-shell atoms, as it derives primarily from excitations to unoccupied orbitals lying relatively close in energy to the ground state, the same is not true for the rare gases. Although other methods have been used to calculate the polarizability of these elements, none of these approaches are based on an *ab initio* technique. As examples of our approach, we calculate the polarizabilities of helium, neon, and argon. In all cases the expression in Eq. (3) will be used as the basic form of the expression for the polarizability α.

A. Helium

For the case of helium the polarized orbitals were produced by expanding the scattering wave function in terms of configurations involving the single replacement of the $1s$ orbital of the target with excitations of the type $1s \rightarrow np$ ($n = 2-5$). For the perturbed continuum state the wave function expansion was over 30 configuration states. The ground state ϕ_0 was determined in two ways [25], either by a single configuration Hartree-Fock calculation or by a multiconfiguration Hartree-Fock calculation. In the former case we obtained a value of $\alpha = 1.506 a_0^3$; in the latter we obtained the value $\alpha = 1.374 a_0^3$. The experimental result [26,27] is $\alpha = 1.384 a_0^3$. The only excitation contributing to the polarization in helium derives from $1s \rightarrow np$. When the Hartree-Fock approximation is used, the $1s$ orbital perceives no influence from other possible configurations, which then seem to appear in the polarizability.

In Table I is given a listing of the contributions of each of the polarized orbitals to the polarizability of helium. These are separated according to whether the HF and or the MCHF calculation was used for the ground state. Energy differences from the corresponding ground state and matrix elements are given as well. Only values for $n = 2$, 3, and 4 are given; the contribution from $n = 5$ is negligible.

B. Neon

For the case of neon it proved to be quite adequate to represent the ground state with only a Hartree-Fock wave function. For the $2s^2 2p^6$ configuration of neon, the polarization effects are taken into account by including configurations involving the single replacement of the target orbitals according to $2s \rightarrow np$ and $2p \rightarrow n'd, n's$. The orbitals np, $n's$, and $n'd$ were varied simultaneously with the continuum. Thirty-eight configurations were used in the distorted wave function expansion for the continuum states. For the calculation of the polarizabili-

TABLE II. Contributions from the polarized orbitals to the static dipole polarizability of neon.

Polarized orbital	ΔE_p (a.u.)[a]	Dipole matrix element	Contribution to $\alpha(a_0^3)$
$3d$	1.566 97	2.073 73	1.830
$4d$	2.041 60	0.629 35	0.129
$5d$	3.844 64	0.464 78	0.037
$3s$	0.835 64	0.871 18	0.605
$4s$	2.900 91	0.222 95	0.011
$5s$	8.557 17	0.034 68	0.0001
$3p$	1.849 08	0.116 07	0.005
$4p$	2.430 63	0.393 20	0.042
$5p$	3.346 85	0.293 53	0.017

Total static dipole polarizability $= 2.676 a_0^3$

[a]Energy difference $E_p - E_0$ from Eq. (3).

TABLE III. Contributions from the polarized orbitals to the static dipole polarizability of argon.

Polarized orbital	ΔE_p (a.u.)[a]	Dipole matrix element	Contribution to α (a_0^3)
$3d$	0.843 91	3.561 38	10.020
$4d$	0.907 64	0.521 98	0.200
$5d$	1.298 31	0.127 14	0.008
$4s$	1.692 20	0.742 03	0.217
$5s$	2.692 20	1.243 68	0.383
$6s$	10.681 54	0.160 96	0.002
$4p$	1.208 10	0.063 38	0.002
$5p$	1.516 79	0.283 69	0.035
$6p$	2.102 92	0.274 20	0.024

Total static dipole polarizability $= 10.891 a_0^3$

[a]Energy difference $E_p - E_0$ from Eq. (3).

TABLE IV. Comparison of various calculations for the dipole polarizability α (in units of a_0^3).

	He	Ne	Ar
Theory			
This work	1.374	2.676	10.891
McEachran, Ryman, and Stauffer (Ref. [30])	1.322	2.377	10.758
Bell, Scott and Lennon (Ref. [31])			12.57
Fon, Berrington, Burke, and Hibbert (Ref. [32])			12.79
Fon, Berrington, and Hibbert (Ref. [33])	1.294		
Fon and Berrington (Ref. [34])		2.555	
Dasgupta and Bhatia (Ref. [35])		2.803	
Dasgupta and Bhatia (Ref. [36])			14.29
Kaneko (Ref. [37])	1.323	2.358	10.60
Lahiri and Mukherji (Ref. [38])	1.323	2.36	10.08
Stevens and Billingsley (Ref. [14])		2.368	
Burke and Mitchell (Ref. [8])			11.56
Experiment			
Leonard and Barker (Ref. [26])	1.384		
Harbatsch, Darrewych, and McEachran (Ref. [28])		2.66	
Miller and Bederson (Ref. [29])			11.06
Dalgarno and Kingston (Ref. [39])			11.08
Dalgarno (Ref. [40])		2.7	

ty we used polarized orbitals generated through the excitations $n=3-5$ and $n'=3-5$. It is found that higher values of n and n' make a negligibly small contribution to the static dipole polarizability.

The contributions to the polarizability from the various polarized orbitals are given in Table II for neon, together with the energy differences from the Hartree-Fock ground state and the matrix elements. The final result which we obtain for the polarizability is $\alpha=2.676a_0^3$. This is in excellent agreement with the experimental result [28] of $\alpha=2.66a_0^3$.

C. Argon

In calculating the polarizability of argon we again used a Hartree-Fock wave function for the ground state. Configurations generated by the single replacement of the orbitals $3s$ and $3p$ according to $3s \rightarrow np$ and $3p \rightarrow n'd, n''s$ with $n=4-6$, $n'=3-5$, and $n''=4-6$ were used to produce the polarized orbitals. The MCHF expansion for the continuum state was over 46 configurations. As was the case for neon, it was found that higher values of n, n', and n'' than those given in Table III made a negligible contribution to the polarizability.

The energy differences, matrix elements, and overall contributions to the polarizability for each of the polarized orbitals are given in Table III for argon. The final result which we obtain for the polarizability is $\alpha=10.891a_0^3$. This, too, is in excellent agreement with the experimental value [29] of $\alpha=11.06a_0^3$.

IV. DISCUSSION

In Table IV is given a comparison of the results of our calculations of the static dipole polarizability with those of other methods. We have already indicated that the results which we obtain agree very well with the experimental values. Thus, even though our original goal had been to produce polarized orbitals to take into account the target polarization in a collision problem, it turns out that the solution to the collision problem at zero energy provides the necessary wave functions for the calculation of the static polarizability, the only *ab initio* calculation to do so.

Because our technique relies on polarized orbitals which are generated as a natural consequence of the solution of the Schrödinger equation through the minimization procedure, the method used is completely general. It can be applied to any atomic system. In addition, it can be generalized in a straightforward way for a given nonzero frequency. It would then be necessary to optimize the orbitals for each frequency separately. This possibility is planned to be explored in a later paper.

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