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Dynamic Polarizability of Helium*

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A variational method is constructed to calculate the dynamic polarizability of the ground state of helium. A 2^1P-type trial function is used for the first-order wave function in computation. The results of the present work agree excellently with the best previous calculations and with experiments in the long-wavelength limit. Furthermore, the present method gives 581 Å for the first transition wavelength as compared with the experimental value 584 Å, while the best previous calculation gives 573 Å.

I. INTRODUCTION

RECENTLY, the interaction between radiation and atomic systems has been investigated extensively using a semiclassical approach.[1–3] The dynamic dipole polarizability of the ground state of helium has been calculated by various methods. The helium system is especially interesting because of its simple structure and because it serves as an excellent test for theories of many-electron atomic systems. Both coupled and uncoupled[4] Hartree-Fock approximations have been used and the results are in good agreement with experiment.

To obtain more accuracy in the theoretical computation, Chan and Dalgarno[5] performed their calculation using a Hylleraas-type zero-order wave function and a product-type first-order wave function. However, the $1^1S \rightarrow 2^1P$ transition wavelength in these calculations always occurs at a wavelength considerably shorter than the true transition wavelength. For example, Chan and Dalgarno's best calculation yields 573 Å, compared to the experimental value 584 Å. The above authors also pointed out that increasing the number of parameters in their trial function does not improve this value significantly. It therefore appears that a more suitable form of first-order wave function is required to obtain better agreement between theoretical calculations and experiment.

Accordingly, Chung and Hurst[6] have used a 2^1P-type first-order wave function to calculate the static polarizability of the ground state of helium. With this form of first-order wave function, the convergence as well as the accuracy are both satisfactory. Therefore, one is led to the supposition that this form of first-order wave function might also yield a more accurate transition wavelength.

In the present work, a variational method is devised to calculate the dynamic polarizability of the ground state of helium. This method will eliminate the necessity of computing the zero- and first-order wave functions in the intermediate steps. In Sec. II, the formulations are derived. In Sec. III, the results of the present work are given and a comparison is made with other calculations.

II. THEORY

If the electric field of radiation is polarized in the z direction, we have[1]

$$\mathcal{E}(t)=2\mathcal{E}_z\cos\omega t=\mathcal{E}_z(e^{i\omega t}+e^{-i\omega t}). \tag{1}$$

Thus, the perturbation potential for a helium atom can be written as

$$\lambda H^1(\mathbf{r},t)=\mathcal{E}_z(z_1+z_2)(e^{i\omega t}+e^{-i\omega t}). \tag{2}$$

Because H^1 has odd parity, the first-order perturbation equation can be written as[7]

$$(H^0-E^0)\Psi^1(\mathbf{r},t)=-H^1(\mathbf{r},t)\psi^0(\mathbf{r})+i\partial\Psi^1(\mathbf{r},t)/\partial t, \tag{3}$$

where

$$(H^0-E^0)\psi^0(\mathbf{r})=0, \tag{3'}$$

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[1] M. Karplus and H. J. Kolker, J. Chem. Phys. **39**, 1493 (1963).

[2] A. Dalgarno and G. A. Victor, Proc. Roy. Soc. (London) **A291**, 291 (1966).

[3] S. Sengupta and A. Mukherji, J. Chem. Phys. **47**, 260 (1967).

[4] M. Karplus and H. J. Kolker, J. Chem. Phys. **39**, 2997 (1963).

[5] Y. M. Chan and A. Dalgarno, Proc. Phys. Soc. (London) **85**, 227 (1965).

[6] Kwong T. Chung and R. P. Hurst, Phys. Rev. **152**, 35 (1966).

[7] Kwong T. Chung, Phys. Rev. **163**, 1343 (1967).

TABLE I. The dynamic polarizability of helium[a] (10^{-24} cm^3).

ω(a.u.)	Wavelength (Å)	16-term ψ^0 [b]	24-term ψ^0 [c]
0.00	∞	0.2046	0.2047
0.050	9112	0.2052	0.2053
0.100	4556	0.2069	0.2070
0.150	3037	0.2099	0.2100
0.200	2278	0.2142	0.2144
0.250	1822	0.2201	0.2203
0.300	1519	0.2278	0.2280
0.350	1302	0.2379	0.2381
0.400	1139	0.2509	0.2511
0.450	1012	0.2679	0.2682
0.500	911	0.2907	0.2910
0.550	828	0.3200	0.3226
0.600	759	0.3659	0.3688
0.650	701	0.4393	0.4429
0.700	651	0.5779	0.5825
0.750	607	0.9527	0.9800
0.800	570	8.2046	$-\infty$
0.850	536	-0.7059	-0.5672

[a] Equations (15) are used.
[b] $\psi_\pm^1$ contain 32 terms each.
[c] $\psi_\pm^1$ contain 48 terms each.

and Ψ^1 is the first-order wave function to be determined.

The solution of Ψ^1 in which we are interested is the steady-state solution, i.e., the perturbation has been turned on for a sufficiently long time and the initial conditions are assumed to be damped out. We thus assume

$$\Psi^1(\mathbf{r},t)=\psi_+^1(\mathbf{r})e^{i\omega t}+\psi_-^1(\mathbf{r})e^{-i\omega t}. \tag{4}$$

Substituting Eq. (4) into (3), one readily obtains

$$(H^0-E^0)\psi_\pm^1=-(z_1+z_2)\psi^0\mp\omega\psi_\pm^1. \tag{5}$$

For the ground state, ψ^0 is real, so that there is no loss of generality in assuming $\psi_\pm^1$ to be real. The following functionals may be constructed from Eq. (5):

$$L_\pm=\langle\psi_\pm^1|H^0-E^0\pm\omega|\psi_\pm^1\rangle+2\langle\psi_\pm^1|z_1+z_2|\psi^0\rangle. \tag{6}$$

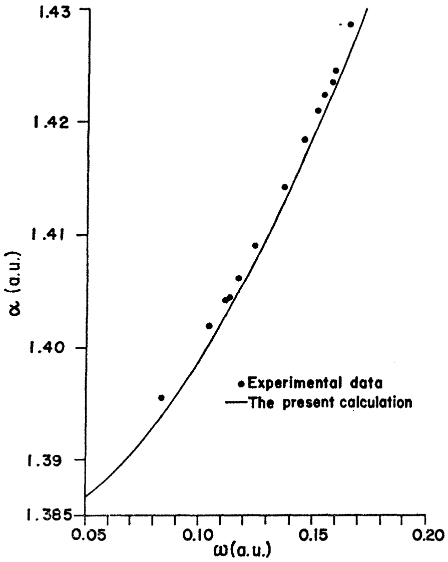

FIG. 1. The dynamic polarizability of the ground state of helium.

The first-order wave functions $\psi_\pm^1$ are approximated by minimizing the functionals $L_\pm$. The dynamic polarizability is then given by

$$\alpha(\omega)=\langle\psi_+^1|z_1+z_2|\psi^0\rangle+\langle\psi_-^1|z_1+z_2|\psi^0\rangle. \tag{7}$$

The usual procedure is first to solve for the zero-order wave function ψ^0, then to solve for $\psi_\pm^1$, and finally to perform the integration indicated by Eq. (7) to obtain the dynamic polarizability. However, a different approach is recommended here.

Consider the functional[8]

$$\begin{aligned}L=\langle\psi^0|H^0-E|\psi^0\rangle+\mathcal{E}_z^2[2\langle\psi^0|z_1+z_2|\psi_+^1\rangle\\ +2\langle\psi^0|z_1+z_2|\psi_-^1\rangle+\langle\psi_+^1|H^0-E^0+\omega|\psi_+^1\rangle\\ +\langle\psi_-^1|H^0-E^0-\omega|\psi_-^1\rangle].\end{aligned} \tag{8}$$

If one minimizes L with respect to ψ^0, ψ_-^1, and ψ_+^1, one obtains

$$\begin{aligned}\delta L=0=2\int\delta\psi^0[(H^0-E)\psi^0+\mathcal{E}_z^2(z_1+z_2)\psi_+^1\\ +\mathcal{E}_z^2(z_1+z_2)\psi_-^1]d\tau+2\mathcal{E}_z^2\int\delta\psi_+^1[(H^0-E^0+\omega)\psi_+^1\\ +(z_1+z_2)\psi_0]d\tau+2\mathcal{E}_z^2\int\delta\psi_-^1[(H^0-E^0-\omega)\psi_-^1\\ +(z_1+z_2)\psi_0]d\tau.\end{aligned} \tag{9}$$

Hence, the solutions for $\psi_\pm^1$ in Eq. (9) are identical to those of Eq. (5). Since $\delta\psi^0$ is arbitrary, we have

$$(H^0-E)\psi^0=-\mathcal{E}_z^2[(z_1+z_2)\psi_+^1+(z_1+z_2)\psi_-^1], \tag{10}$$

where[9]

$$E=E^0-\Delta E. \tag{11}$$

Multiplying Eq. (10) by ψ^0 and integrating over all space, one obtains immediately

$$\begin{aligned}-\Delta E/\mathcal{E}_z^2=\langle\psi^0|z_1+z_2|\psi_+^1\rangle\\ +\langle\psi^0|z_1+z_2|\psi_-^1\rangle=\alpha(\omega),\end{aligned} \tag{12}$$

where Eq. (7) is used. In other words, one can obtain α from the solution of the "secular equation" indicated by Eq. (8).

By the same reasoning, one can also construct two independent functionals from Eq. (8), so that the computations can be performed using independent linear parameters in ψ_+^1 and ψ_-^1, i.e.,

$$\begin{aligned}L_\pm=\langle\psi^0|H^0-E^\pm|\psi^0\rangle+\mathcal{E}_z^2[2\langle\psi^0|z_1+z_2|\psi_\pm^1\rangle\\ +\langle\psi_\pm^1|H^0-E^0\pm\omega|\psi_\pm^1\rangle]\end{aligned} \tag{13}$$

and

$$\alpha(\omega)=(2E^0-E^+-E^-)/\mathcal{E}_z^2. \tag{14}$$

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[8] $\mathcal{E}_z$ is introduced only for computational convenience.

[9] Here ΔE does not have its usual meaning of perturbation energy.

III. METHOD OF COMPUTATION AND RESULTS

In computing the dynamic polarizability of helium, one uses as the trial function the Hylleraas-type wave function

$$\psi^0=\sum_{i=1}^{N} c_i e^{-s/2} s^{l_i} u^{m_i} t^{n_i}. \tag{15a}$$

The $\psi_\pm^1$ both take the form

$$\psi^1=\sum_{i=1}^{N} d_i (z_1 \pm z_2) e^{-s/2} s^{l_i} u^{m_i} t^{n_i}, \tag{15b}$$

where

$$s=r_1+r_2, \quad u=r_{12}, \quad t=r_1-r_2. \tag{15c}$$

Here, the n_i are chosen such that the spatial wave function is always symmetric. To increase the flexibility of the variational function a scaling factor is also used.[6]

In the first calculation, we used a 16-term zero-order wave function, while $\psi_\pm^1$ each contained 32 terms. Although this computation yielded an accurate polarizability in the long-wavelength region, the transition wavelength of $1^1S \rightarrow 2^1P$ is off by 3.7%. Next, we extended the zero-order wave function to 24 terms and $\psi_\pm^1$ to 48 terms each. The transition frequency was then off by 2.47%. This improvement was small, and the rate of convergence is not quite satisfactory. The results of these two computations are given in Table I.

To improve the rate of convergence, another form of trial wave function[10] was employed, namely,

$$\psi^0=\sum_{i=1}^{N} c_i e^{-cs/2} s^{l_i} u^{m_i} t^{n_i} \begin{Bmatrix} \sinh\frac{1}{2}t \\ \cosh\frac{1}{2}t \end{Bmatrix}, \tag{16a}$$

and

$$\psi^1=\sum_{i=1}^{N} d^i e^{-cs/2} (z_1 \pm z_2) s^{l_i} u^{m_i} t^{n_i} \begin{Bmatrix} \sinh\frac{1}{2}t \\ \cosh\frac{1}{2}t \end{Bmatrix}. \tag{16b}$$

Here the coefficients c are determined[6] by minimizing E^0, and the exponents n_i are chosen so that the spatial wave function is symmetric. Computations have been performed for ψ^0 with 32 terms and $\psi_\pm^1$ with 64 terms. The transition wavelength is 581.2 Å. Compared to the experimental value of 584 Å, this is an error of approximately 0.5%. Experiments by Cuthbertson and Cuthbertson[11] (1932) measured the refractive index of helium over the range 2753 to 5462 Å. Their results exceeded the results of the calculations of Chan and Dalgarno by approximately 0.5%. This discrepancy is significantly improved in the present work. A comparison of the present work with the experiment is shown in Fig. 1. The average deviation is approximately 0.05%. Table II shows a comparison of the present calculations with those of Dalgarno and Victor and Chan and Dalgarno. It seems the calculations performed using the method described herein yield the best results obtained to date.

TABLE II. Calculations of the dynamic polarizability of helium (10^{-24} cm^3).

ω (a.u.)	Coupled HF[a]	Chan and Dalgarno[b]	Present work[c]
0.00	0.196	0.204	0.2051
0.05	0.196	0.205	0.2055
0.10	0.198	0.207	0.2073
0.15	0.201	0.210	0.2103
0.20	0.205	0.214	0.2146
0.25	0.210	0.220	0.2206
0.30	0.217	0.227	0.2283
0.35	0.226	0.237	0.2385
0.40	0.237	0.250	0.2516
0.45	0.252	0.267	0.2689
0.50	0.272	0.289	0.2920
0.55	0.299	0.320	0.3241
0.60	0.337	0.366	0.3718
0.65			0.4502
0.70			0.6091
0.75			1.1808
0.77			2.4994
0.78			8.3127
0.782			17.2570
0.784			−143.5672
0.79			−4.5561
0.80			−1.5306

[a] A. Dalgarno and G. A. Victor, Proc. Roy. Soc. (London) **A291**, 291 (1966).

[b] Y. M. Chan and A. Dalgarno, Proc. Phys. Soc. (London) **85**, 227 (1965).

[c] ψ^0 contains 32 terms; $\psi_\pm^1$ contain 64 terms each; Eqs. (16) are used.

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[10] This ψ^0 is certainly not the best choice; instead, it is chosen for computational convenience. In the present calculation, it gives $E^0=2.903717$ atomic units (a.u.), as compared with $E^0=2.903724$ a.u. of Pekeris.

[11] C. Cuthbertson and M. Cuthbertson, Proc. Roy. Soc. (London) **A135**, 40 (1932).