Diamagnetic form factors in photon-atom scattering and higher-multipole Casimir effect in heliumlike Rydberg ions

C. K. Au
Physics Department, University of South Carolina, Columbia, South Carolina 29208 and Lewes Centre for Physics, Lewes, Delaware 19958*
(Received 6 August 1984)

We examine the electric and magnetic form factors in the nonrelativistic on-shell photon-atom scattering amplitude both with and without retardation and with and without spin. We show that to the extent that we neglect hyperfine splitting compared to ordinary atomic-level separations, the Pauli spin interaction with the photon field leads only to a magnetic form factor even with the inclusion of retardation. On the other hand, the radiation Hamiltonian in the minimal-coupling scheme leads to both electric and magnetic form factors when retardation is included. However, if the scattering atom is in a rotationally invariant S state, we can show that the electric and magnetic form factors are not independent when spin is neglected. This observation is then discussed along with the higher-multipole contributions to the retarded long-range potential between a pair of spinless neutral atoms and in Rydberg states between the core and the outer electron. When the atoms and the core ions in the Rydberg atoms involved are hydrogenic, another relation occurs because of O_4 symmetry in hydrogen when spin is neglected. In this case it becomes possible to express all derivatives with respect to the 4-momentum transfer square t of the electric and magnetic spectral functions in terms of the electric spectral function at zero t, which is in turn expressible in terms of hydrogen dipole oscillator strengths. It is thus possible to express all nonrelativistic higher multipole contributions to the retarded long-range interaction due to two-photon exchange between a pair of hydrogenic atoms or in heliumlike Rydberg atoms in terms of hydrogenic dipole oscillator strength sum rules.

INTRODUCTION

In a classic paper, Cassimir and Polder[1] showed that when retardation is properly taken into account, the van der Waals potential between two neutral spinless atoms falls with the distance of separation between the two atoms as R^{-7} at large distances, in contrast to the R^{-6} behavior in the London form.[2] To lowest order in perturbation theory, the van der Waals interaction arises from the exchange of two photons between the two atoms. This two-photon exchange effect has been studied by Feinberg and Sucher[3] in a covariant model-independent manner using a field-theoretic dispersion technique. This approach puts electric and magnetic effects on equal footing. As a result, Feinberg and Sucher obtain a generalized form of the Casimir-Polder potential. This is expressible in terms of the spectral functions of the electric and magnetic form factors in the photon scattering amplitudes for the respective atoms. Later, the higher-multipole contribution to the retarded van der Waals potential between two spinless neutral atoms was studied by Au and Feinberg.[4] It is found that these higher-multipole contributions are expressible in terms of the derivatives with respect to the invariant 4-momentum transfer square t of the electric and magnetic spectral functions.

In a later analysis, Feinberg[5] showed that the best candidate to observe these retardation effects is in two superconducting spheres. Even there, the effects is probably not observable within present-day experimental accuracy. Thus, there is practically no hope of observing these retardation effects in a pair of atoms. However, recent precision laser experiments on high-Rydberg states in helium and future aspects of performing similar experiments in high-Z heliumlike ions seem to indicate that detection of these retardation effects may be possible.[6] The computation of these retarded long-range interactions in Rydberg atoms can be carried out between a charged particle and a neutral system according to the results of Feinberg and Sucher.[7] Such a calculation, to the leading order in the dipole approximation has been carried out for helium and heliumlike ions, with the core taken to be a hydrogenic ion without spin.[8] As experimental accuracy improves, it seems desirable that other corrections be looked at more closely and among these are the higher-multipole contributions. The higher-multipole contributions to the retarded long-range interaction in Rydberg atoms can be expressed in terms of the derivatives with respect to t of the electric and magnetic spectral functions. In general, the electric and magnetic form factors are independent quantities. However, we shall show in the present paper that when spin is neglected, the magnetic form factor in the elastic photon scattering amplitude from an atom in a rotationally invariant S state is in fact not independent of the electric form factor. Thus in a calculation of the van der Waals interaction where spin is neglected for a pair of spinless atoms or for heliumlike Rydberg states, the electric and magnetic effects are not independent and it is in fact possible to reduce the expression for these higher-multipole contributions to a form involving the independent form factors alone. In this form, it is easier to esti-

mate the relative contribution from each multipole of electric or magnetic origin. In the case where the atoms or the core ions in Rydberg states involved are hydrogenic, another relation between the successive t derivatives of the form factors exists because of the O_4 symmetry in hydrogen. It is then possible to express all multipole contributions, when spin is neglected, in terms of the electric spectral function at zero momentum transfer. Furthermore, this $\rho_E(\omega, t=0)$ is computable analytically with use of the Coulomb Green's function and the result is expressed in terms of the hydrogenic dipole oscillator strengths. This indicates that all nonrelativistic higher-multipole retardation effects in heliumlike Rydberg atoms are easily computable in terms of dipole sum rules. The inclusion of spin and other relativistic corrections are also, in principle, manageable. However we do not deal with these other effects in the present paper.

The scheme of the present paper is as follows. In Sec. I we review the covariant results of Feinberg and Sucher on the on-shell photon scattering amplitude by a spinless particle. We then reduce the results to those in the rest frame of the neutral particle which is taken to be a massive atom. We give the relation between the electric and magnetic form factors and the scattering amplitude. In Sec. II we show that the Pauli interaction with the photon field only leads to a magnetic form factor to the extent that we neglect hyperfine splitting compared to ordinary atomic-level splitting, even when retardation is included. In Sec. III we show that in the minimal-coupling scheme for the radiation Hamiltonian, the seagull interaction contributes only to the real part of the electric form factor and hence makes no contribution to the spectral function at all. The $\mathbf{p}\cdot\mathbf{A}$ interaction, in the dipole approximation, gives rise only to the electric form factor and for photon scattering by atoms in the ground state, only the direct graph gives an imaginary part and hence contributes to the spectral function. When retardation is included in the $\mathbf{p}\cdot\mathbf{A}$ interaction, a magnetic form factor as well as an electric form factor occur. However, if the scattering atom is in a rotationally invariant S state, the magnetic and electric form factors are not independent. Consequently the number of quantities that we need to describe the higher-multipole retarded van der Waals interaction is reduced by half, although the total number is still infinite if we want to include all multipoles. In Sec. IV we give the expressions for these retarded higher-multipole long-range interactions in Rydberg atoms in terms of these independent quantities and make an estimate of their relative contributions. In Sec. V we show that if the atom or core ion involved is indeed hydrogenic without spin, another simplification occurs because of the O_4 symmetry. It is then possible to express all multipole contributions in terms of the electric form factor at zero momentum transfer, which in turn is expressible in terms of the hydrogenic dipole oscillator strengths. Thus in principle, we have shown that it is possible to calculate all nonrelativistic higher-multipole contributions to the retarded long-range interaction due to two-photon exchange between a pair of spinless hydrogenic ions or in heliumlike Rydberg atoms where spin is neglected in terms of hydrogenic dipole oscillator sum rules. In Sec. VI we give the leading energy corrections in He Rydberg states (for $n=10$) due to retarded electric quadrupole and diamagnetic dipole interactions.

I. E AND M FORM FACTORS AND THE PHOTON SCATTERING AMPLITUDE

We consider the scattering of a photon with 4-momentum $k=(\mathbf{k},\omega)$ and polarization ϵ by a spinless neutral system with 4-momentum p into the photon state $|k',\epsilon'\rangle$ and system momentum state p' as in Fig. 1. For real photons, it is shown by Feinberg and Sucher that the invariant amplitude M for this scattering is given by[3]

$$M=M_{\mu\nu}\epsilon_\mu\epsilon'_\nu \ , \tag{1.1}$$

where

$$M_{\mu\nu}=-\sum_{a=1,2} T_{a;\mu\nu}F_a \ , \tag{1.2}$$

$$T_{1;\mu\nu}=(k\cdot P)(k'\cdot P)g_{\mu\nu}+(k\cdot k')P_\mu P_\nu-(k\cdot P)k'_\mu P_\nu -(k'\cdot P)k_\nu P_\mu \ , \tag{1.3}$$

$$T_{2;\mu\nu}=(k\cdot k')g_{\mu\nu}-k_\nu k'_\mu \ , \tag{1.4}$$

$$P=(p+p')/m_0 \ , \tag{1.5}$$

and m_0 is the mass of the spinless neutral system, hereafter referred to as the atom. In the rest frame of the massive atom and choosing the particular gauge that the time component of the polarization vector vanishes, we have

$$p=p'=(0,m_0) \ , \tag{1.6}$$

$$P=(0,2) \ , \tag{1.7}$$

$$\epsilon=(\epsilon,0), \quad \epsilon'=(\epsilon',0) \ , \tag{1.8}$$

and

$$\epsilon_\mu P_\mu=0=\epsilon'_\mu P_\mu \ . \tag{1.9}$$

On substituting Eqs. (1.6)—(1.9) into Eqs. (1.1)—(1.5), the invariant amplitude is then expressed in terms of the form factors F_1 and F_2 by

$$M=(4F_1+F_2)\omega\omega'(\epsilon\cdot\epsilon')+F_2[(\mathbf{k}\cdot\epsilon')(\mathbf{k}'\cdot\epsilon)-(\mathbf{k}\cdot\mathbf{k}')(\epsilon\cdot\epsilon')] \ . \tag{1.10}$$

The electric and magnetic form factors F_E and F_M are

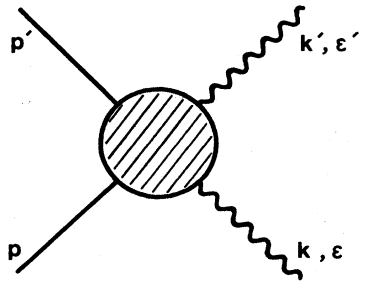

FIG. 1. The elastic scattering of a photon with momentum k and polarization ϵ by a spinless particle with momentum p into the photon state with momentum k' and polarization ϵ' and particle momentum state p'.

defined in terms of F_1 and F_2 by[3]

$$F_E \equiv -(4F_1+F_2)/2m_0 \tag{1.11}$$

and

$$F_M \equiv F_2/2m_0 \ . \tag{1.12}$$

The scattering amplitude in the c.m. frame (in this case, the rest frame of the massive atom) is related to the invariant on-shell amplitude by

$$f = M/8\pi W = M/8\pi m_0 \ , \tag{1.13}$$

where W is the total energy in the atom-photon channel, which for a massive atom is just the atomic mass. Upon using Eqs. (1.10)—(1.12) in Eq. (1.13), we have

$$4\pi f = (F_E + F_M \cos\theta)\omega\omega'(\boldsymbol{\epsilon}\cdot\boldsymbol{\epsilon}') - F_M(\mathbf{k}\cdot\boldsymbol{\epsilon}')(\mathbf{k}'\cdot\boldsymbol{\epsilon}) \ , \tag{1.14}$$

where θ is the photon scattering angle. On the other hand, from general rotational-invariance arguments applied to the Kramers-Heisenberg-Waller (KHW) matrix element, the elastic scattering amplitude ($\omega=\omega'$) is given by

$$f(\omega,\theta) = \epsilon_i \epsilon_j' [A(\omega\theta)\delta_{ij} + \omega^2 B(\omega,\theta)\hat{k}_i' \hat{k}_j] \ . \tag{1.15}$$

On comparing Eq. (1.14) and Eq. (1.15), we deduce

$$F_M = -4\pi B \ , \tag{1.16}$$

and

$$F_E = \frac{4\pi}{\omega^2}(A + B\omega^2 \cos\theta) \ . \tag{1.17}$$

In the dipole approximation without electron spin, there is no $\mathbf{k}$ dependence in the KHW matrix element and so B is zero. In the next section we shall show that the Pauli electron-spin interaction contributes only to a magnetic form factor. When retardation is included in the absence of electron spin, B is no longer zero and so there is a magnetic form factor. This has been previously designated as the diamagnetic form factor. However, as we shall show in a subsequent section, for the scattering of photon by an atom in an S state without electron spin, B and A are not independent. Thus, in effect, there is only one form factor.

II. CONTRIBUTION TO E AND M FORM FACTORS FROM THE SPIN INTERACTION

The interaction Hamiltonian for the emission and absorption of photons by atoms is according to the Pauli theory of electron spin and the minimal-coupling scheme

$$H_{\text{int}} = H_{\text{spatial}} + H_{\text{spin}} \ , \tag{2.1}$$

$$H_{\text{spatial}} = (-e/m)\mathbf{p}\cdot\mathbf{A} + e^2A^2/2m^2 \ , \tag{2.2}$$

$$H_{\text{spin}} = \mu_B \boldsymbol{\sigma}\cdot\boldsymbol{\nabla}\times\mathbf{A} \ , \tag{2.3}$$

where μ_B is the Bohr magneton and σ is the Pauli spin matrix. The interaction of the photon field with the nuclear magnetic moment is about 2000 times smaller and is neglected. The elastic scattering amplitude corresponding to H_{spin} is

$$f_{\text{spin}} \sim \epsilon_{ijl}\epsilon_{\alpha\beta\gamma} k_j' \epsilon_l' k_\beta \epsilon_\gamma \sum_{n,\rho} \frac{\langle 0|\sigma_i|S_{n\rho}\rangle\langle S_{n\rho}|\sigma_\alpha|0\rangle\langle 0|e^{i\mathbf{k}'\cdot\mathbf{x}}|R_{n\rho}\rangle\langle R_{n\rho}|e^{-i\mathbf{k}\cdot\mathbf{x}}|0\rangle}{E_0 - E_{n\rho} + \omega} + (\omega \leftrightarrow -\omega) \ , \tag{2.4}$$

where we have used the pair of indices $n\rho$ to denote the intermediate states with n referring to the spatial part and ρ referring to the spin part. To a very good approximation, the wave function factorizes into a spin part and a spatial part and so $S_{n\rho}$ depends only on ρ and $R_{n\rho}$ depends only on n. Furthermore if one neglects hyperfine splitting compared to ordinary atomic-level splittings, $E_{n\rho}$ depends only on n and the sum in Eq. (2.4) factorizes to

$$f_{\text{spin}} \sim \epsilon_{ijl}\epsilon_{\alpha\beta\gamma} k_j' \epsilon_l' k_\beta \epsilon_\gamma T_{i\alpha} S \ , \tag{2.5}$$

where

$$T_{i\alpha} = \sum_\rho \langle 0|\sigma_i|S_\rho\rangle\langle S_\rho|\sigma_\alpha|0\rangle \ , \tag{2.6}$$

and

$$S = \sum_n \frac{\langle 0|e^{i\mathbf{k}'\cdot\mathbf{x}}|R_n\rangle\langle R_n|e^{i\mathbf{k}\cdot\mathbf{x}}|0\rangle}{E_0 - E_n + \omega} + (\omega \leftrightarrow -\omega) \ . \tag{2.7}$$

From the rotational invariance of the state $|0\rangle$, the quantity S must be a scalar quantity that depends only on ω and the scattering angle θ. In the case of hydrogenic atoms, the frequency-dependent sum rule in Eq. (2.7) has been evaluated.[9] On using closure for the spin states in the sum in Eq. (2.6), we find

$$T_{i\alpha} = \langle 0|\sigma_i\sigma_\alpha|0\rangle = \delta_{i\alpha} \ . \tag{2.8}$$

Hence

$$f_{\text{spin}} = S(\omega,\theta)[(\mathbf{k}\cdot\mathbf{k}')(\boldsymbol{\epsilon}\cdot\boldsymbol{\epsilon}') - (\mathbf{k}\cdot\boldsymbol{\epsilon}')(\mathbf{k}'\cdot\boldsymbol{\epsilon})] \tag{2.9}$$

and thus according to Eqs. (1.16) and (1.17)

$$F_{M,\text{spin}} = 4\pi S(\omega,\theta) \ , \tag{2.10}$$

and

$$F_{E,\text{spin}} = 0 \ . \tag{2.11}$$

III. CONTRIBUTION TO E AND M FORM FACTORS FROM THE SPATIAL INTERACTION

We now turn to the spatial part of the interaction Hamiltonian. First, we note that the seagull term ($\sim A^2$), $H_{\text{spatial}2}$, can only lead to an electric form factor. It is essentially the Fourier transform of the square of the atomic wave function. Furthermore, rotational invariance of the initial atomic state requires that this be a function of $(\mathbf{k}-\mathbf{k}')^2$ and consequently must be real since the factor i appears only in conjunction with $(\mathbf{k}-\mathbf{k}')$. Thus the seagull part does not contribute to the absorptive part but

only to the dispersive part of the electric form factor.

Next, we examine the contribution from $H_{\text{spatial 1}}$, the part of H_{spatial} that is linear in $\mathbf{A}$ (the $\mathbf{p}\cdot\mathbf{A}$ term). To lowest order in perturbation theory to account for the scattering process, the scattering amplitude is given by

$$f_{\text{spatial 1}} \sim \sum_n \frac{\langle 0 | (\epsilon'\cdot\mathbf{p}) e^{-i\mathbf{k}'\cdot\mathbf{x}} | n \rangle \langle n | (\epsilon\cdot\mathbf{p}) e^{i\mathbf{k}\cdot\mathbf{x}} | 0 \rangle}{E_0 - E_n + \omega} + (\omega \leftrightarrow -\omega) \tag{3.1}$$

$$\equiv \epsilon'_\alpha \epsilon_\beta \langle 0 | p_\alpha e^{-i\mathbf{k}'\cdot\mathbf{x}} G p_\beta e^{i\mathbf{k}\cdot\mathbf{x}} | 0 \rangle + (\omega \leftrightarrow -\omega) \tag{3.2}$$

$$\equiv \epsilon'_\alpha \epsilon_\beta W_{\alpha\beta} + (\omega \leftrightarrow -\omega) \tag{3.3}$$

which are the direct and crossed terms of the KHW matrix elements. In the case we are considering where $|0\rangle$ is the ground state, only the direct term can have an imaginary part and hence contribute to the absorptive part of the form factors. To study the contribution of the KHW matrix element to the electric and magnetic form factors, it is best to look at it in the momentum representation since the inclusion of retardation in the KHW matrix element is then equivalent to the displacement by the amount of photon momentum. We also see that we are free to commute the retardation factor with the momentum operator because of the transversality of the photon. Hence, the direct term of the KHW matrix element can be written as

$$\epsilon'_\alpha \epsilon_\beta W_{\alpha\beta} = \epsilon'_\alpha \epsilon_\beta \int\int d\mathbf{p}\, d\mathbf{p}'\, p'_\alpha F_b^*(\mathbf{p}'-\mathbf{k}') \times G(\mathbf{p},\mathbf{p}',\omega) p_\beta F_a(\mathbf{p}-\mathbf{k}) , \tag{3.4}$$

where a and b denote the initial and final states and are equal to each other in elastic scattering. The Green's function G in Eq. (3.4) is rotationally invariant and since it measures the response at $\mathbf{p}'$ due to a disturbance at $\mathbf{p}$, G must be a function of p^2, p'^2, $(\mathbf{p}-\mathbf{p}')^2$, and ω. From the structure of Eq. (3.1), ω must enter only as a parameter. Furthermore, if both a and b are rotationally invariant states, F_a and F_b must be functions of $(\mathbf{p}-\mathbf{k})^2$ and of $(\mathbf{p}'-\mathbf{k}')^2$. Thus Eq. (3.4) can be rewritten as

$$\epsilon'_\alpha \epsilon_\beta W_{\alpha\beta} = \epsilon'_\alpha \epsilon_\beta \int\int d\mathbf{p}\, d\mathbf{p}'\, p'_\alpha p_\beta F_b^*((\mathbf{p}'-\mathbf{k}')^2) \times G(p^2,p'^2,(\mathbf{p}-\mathbf{p}')^2,\omega) \times F_a((\mathbf{p}-\mathbf{k})^2) \tag{3.5}$$

$$= \tfrac{1}{4}\epsilon'_\alpha \epsilon_\beta \frac{\partial}{\partial k'_\alpha}\frac{\partial}{\partial k_\beta} \int\int d\mathbf{p}\, d\mathbf{p}'\, F_b^*((\mathbf{p}'-\mathbf{k}')^2) \times G F_a((\mathbf{p}-\mathbf{k})^2) , \tag{3.6}$$

where we have made explicit use of the transversality condition $\epsilon\cdot\mathbf{k}=0=\epsilon'\cdot\mathbf{k}'$. It is then obvious that the double integral over $\mathbf{p}$ and $\mathbf{p}'$ gives a function of k^2, k'^2, $(\mathbf{k}-\mathbf{k}')^2$, and ω. We shall denote this function by J. For elastic scattering, $-(\mathbf{k}-\mathbf{k}')^2$ is equal to t, the invariant 4-momentum transfer squared for the scattering process. Therefore we have

$$\epsilon'_\alpha \epsilon_\beta W_{\alpha\beta} = \tfrac{1}{4}\epsilon'_\alpha \epsilon_\beta \frac{\partial}{\partial k'_\alpha}\frac{\partial}{\partial k_\beta} J(t,k^2,k'^2,\omega) \tag{3.7}$$

$$= \epsilon'_\alpha \epsilon_\beta [-J_{tt}(k_\alpha - k'_\alpha)(k_\beta - k'_\beta) + \tfrac{1}{2} J_t \delta_{\alpha\beta}] \tag{3.8}$$

$$= \tfrac{1}{2} J_t (\epsilon'\cdot\epsilon) + J_{tt}(\epsilon'\cdot\mathbf{k})(\epsilon\cdot\mathbf{k}') , \tag{3.9}$$

where again we have made explicit use of the traversality condition. In Eqs. (3.8) and (3.9) a subscript t indicates a partial derivative with respect to t.

The above results imply that the electric form factor and the diamagnetic form factor are not independent. Moreover, since the seagull interaction term and the crossed term do not contribute to the absorptive part, when expressed as a power series in t, the electric spectral function bears a simple relation to the diamagnetic spectral function. We express these as

$$\mathrm{Im} F_E(\omega,t) = \rho_E(\omega,t) \equiv \sum_{n=0}^{\infty} \rho_{E,n}(\omega) t^n , \tag{3.10}$$

and

$$\mathrm{Im} F_M(\omega,t) = \rho_M(\omega,t) \equiv \sum_{n=0}^{\infty} \rho_{M,n}(\omega) t^n . \tag{3.11}$$

If we neglect the spin interaction, then it follows from Eqs. (1.15)–(1.17) that

$$\rho_{E,n} = \frac{4\pi}{\omega^2} \mathrm{Im} \left[P_n + Q_n + \frac{Q_{n-1}}{2\omega^2} \right] , \tag{3.12}$$

and

$$\rho_{M,n}^{\text{dia}} = \frac{-4\pi}{\omega^2} \mathrm{Im} Q_n , \tag{3.13}$$

where the P_n's and Q_n's are defined by

$$A(\omega,\theta) \equiv \sum_{n=0}^{\infty} P_n t^n , \tag{3.14}$$

$$\omega^2 B(\omega,\theta) \equiv \sum_{n=0}^{\infty} Q_n t^n . \tag{3.15}$$

But from Eq. (3.9), we see that

$$\mathrm{Im} A(\omega,\theta) = \tfrac{1}{2} \mathrm{Im} J_t , \tag{3.16}$$

and

$$\mathrm{Im}\omega^2 B(\omega,\theta) = \mathrm{Im} J_{tt} \omega^2 . \tag{3.17}$$

Hence we have

$$\mathrm{Im} P_n = \mathrm{Im} Q_{n-1}/2n\omega^2, \quad n \geq 1 . \tag{3.18}$$

Therefore, we see that the independent quantities that we need to determine the spectral functions $\rho_{E,n}$ and $\rho_{M,n}^{\text{dia}}$ are just the $\mathrm{Im} P_i$'s for $i = 0, 1, \ldots, \infty$. Alternatively from Eqs. (3.12) and (3.13), the independent quantities are $\rho_{E,0}$ and $\rho_{M,n}^{\text{dia}}$, $n = 0, 1, \ldots, \infty$. For $n \geq 1$, $\rho_{E,n}$ can be expressed in terms of the diamagnetic spectral functions

$$\rho_{E,n} = -\frac{1}{2\omega^2}\frac{n+1}{n} \rho_{M,n-1} - \rho_{M,n} , \tag{3.19}$$

where here and henceforth we drop the superscript dia, since without spin interaction the only contribution to the magnetic form factor is from the diamagnetic part. From Eq. (3.19), on using a dispersion relation, we obtain

$$F_{E,n}(\omega)=-\frac{n+1}{2n\omega^2}[F_{M,n-1}(\omega)-F_{M,n-1}(0)] -F_{M,n}(\omega)\ . \tag{3.20}$$

IV. HIGHER-MULTIPOLE CONTRIBUTIONS TO THE RETARDED VAN DER WAALS POTENTIAL

It has been shown earlier[4] that the higher-multipole contribution to the retarded van der Waals potential between a pair of spinless atoms A_1 and A_2 are expressible in terms of the $\rho_{X,n}$'s ($X=E$ or M) for the atoms A_1 and A_2. The retarded van der Waals interaction between a pair of spinless atoms is not likely to be detectable,[5] not to mention the higher-multipole contributions. However, recent precision laser experiments[6] on the high-Rydberg states in helium as well as possible similar experiments on heliumlike ions of high Z seem to indicate that such retardation effects may actually be observable. In fact, we have shown that for helium, the inclusion of retardation[8] leads to corrections to the existing theoretical results without retardation[10] that are of the order of the discrepancies from experimentally measured values[6] within experimental errors. This clearly indicates that at some point, the inclusion of retarded higher-multipole long-range interaction in the calculation of the spectrum of heliumlike Rydberg states is desirable. The higher-multiple contributions to the retarded van der Waals potential in the high-Rydberg states are likewise expressible in terms of integrals of the $\rho_{X,n}$'s. Our analysis in the previous section has shown that when electron spin is ignored, the magnetic and electric form factors are not independent and in fact expressible in terms of $\rho_{E,0}$ and $\rho_{M,n}$. In view of this, it seems appropriate to express these higher-multipole retarded van der Waals potential in terms of the independent form factors. A similar procedure can be carried out for the higher-multipole retarded van der Waals potential between a pair of spinless neutral atoms. However, this will not be attempted here.

The retarded two-photon exchange potential between a neutral atom and an electron is given by Feinberg and Sucher as[7]

$$V_{2\gamma}(R)=-\tfrac{1}{2}\alpha\sum_{n=0}^{\infty}\alpha_{E,2^{n+1}}(0)/R^{4+2n} +\sum_X\sum_{n=0}^{\infty}\xi_X\alpha_{X,2^{n+1}}(0)\frac{2n+3}{3}\Big/R^{5+2n} +\frac{\alpha\lambda\!\!\!^{-}}{16\pi^2R}\sum_X\sum_{n=0}^{\infty}\frac{d^{2n}}{dR^{2n}} \times\int_0^{\infty}dk\frac{1}{\pi}\frac{\rho_{X,n}(k)}{kR^4}J_X(kR)\ , \tag{4.1}$$

where the sum over X is taken over E and M, and $\alpha_{X,2^{n+1}}(0)$ is the static electric or magnetic multipole polarizability which is related to the t derivatives of the E and M form factors at zero frequency by

$$\alpha_{X,2^{n+1}}(0)=\frac{(2n+2)^{1/4}}{8\pi}F_{X,n}(0)\ , \tag{4.2}$$

$$F_{X,n}(k)=\frac{1}{n!}\frac{d^n}{dt^n}F_X(k,t)\bigg|_{t=0}\ , \tag{4.3}$$

$$\xi_E=\frac{11}{4\pi}\alpha\lambda\!\!\!^{-}\ , \tag{4.4}$$

$$\xi_M=\frac{5}{4\pi}\alpha\lambda\!\!\!^{-}\ , \tag{4.5}$$

$\lambda\!\!\!^{-}$ is the electron Compton wavelength,

$$\lambda\!\!\!^{-}=\hbar/mc\ , \tag{4.6}$$

$$J_E(z)=\frac{8}{z}[(3-5z^2+z^4)f(2z)+(6z-2z^3)g(2z) +\tfrac{13}{4}z-\tfrac{1}{2}z^3]\ , \tag{4.7}$$

$$J_M(z)=\frac{8}{z}[(z^2-z^4)f(2z)+2z^3g(2z)-\tfrac{5}{4}z+\tfrac{1}{2}z^3]\ , \tag{4.8}$$

f and g are the auxillary functions for the sine and cosine integrals

$$f(z)=-\cos z\,\mathrm{si}(z)+\sin z\,\mathrm{Ci}(z)\ , \tag{4.9}$$

$$g(z)=-\mathrm{Ci}(z)\cos z-\mathrm{si}(z)\sin z\ , \tag{4.10}$$

and α is the fine-structure constant. The first term in Eq. (4.1) is the classical multipole interaction term between the electron and the neutral atom. The second term in Eq. (4.1) is the electric and magnetic multipole analog of the interaction found by Kelsey and Spruch[11] and by Bernabeu and Tarrach.[12] According to the results in the last section, when electron spin is neglected, the third term in Eq. (4.1) can be expressed in terms of $\rho_{E,0}$ and $\rho_{M,n}$. Specifically, we write

$$\sum_X\sum_{n=0}^{\infty}\frac{d^{2n}}{dR^{2n}}\int_0^{\infty}dk\frac{1}{\pi}\frac{\rho_{X,n}(k)}{kR^4}J_X(kR)=\int_0^{\infty}dk\frac{1}{\pi kR^4}[\rho_{E,0}(k)J_E(kR)+\rho_{M,0}(k)J_M(kR)] +\sum_{n=1}^{\infty}\frac{d^{2n}}{dR^{2n}}\int_0^{\infty}dk\frac{1}{\pi kR^4}\bigg[\rho_{M,n}(k)J_M(kR)-\rho_{M,n}(k)J_E(kR) -\frac{n+1}{2nk^2}\rho_{M,n-1}(k)J_E(kr)\bigg]\ . \tag{4.11}$$

It is interesting to estimate the relative magnitude of the various terms in Eq. (4.11). The first term is due to the dominant electric dipole interaction. The second term is due to the diamagnetic dipole interaction and is expected to be smaller than the first term by order $(Z\alpha)^2$. The fifth (last) term is dominated by the electric multipole interaction and it is smaller than the first term by order $(a/R)^{2n}$ where a is the size of the atom. The third and fourth term are comparable in magnitude and are of order $(Z\alpha)^2$ compared to the last term.

V. HIGHER-MULTIPOLE CONTRIBUTIONS TO THE RETARDED VAN DER WAALS POTENTIAL IN He-LIKE RYDBERG STATES

The results derived in the previous sections are, in general, valid for atomic S states when electron spin is neglected without any reference to the atomic structure. In He-like Rydberg states, the core is a hydrogenic ion. When spin is neglected, the nonrelativistic elastic scattering amplitude of photon by a hydrogenic ion of charge Z can be evaluated in closed form by using the Coulomb Green's-function method.[13] The general results derived in the earlier sections are all borne out by the analytic expressions for the scattering amplitude. In addition, because of O_4 symmetry in hydrogen, there is a simple relation between the successive P_n's and Q_n's as defined in Eqs. (3.14) and (3.15). This relation is even simpler for the imaginary part and can be written as[13]

$$\frac{\mathrm{Im}P_{q+1}(\omega)}{\mathrm{Im}P_q(\omega)}=\frac{\Phi}{\tau^2}\left[\frac{a}{Z}\right]^2\frac{(2+q)^2(\tau-1)+1}{(q+5/2)(q+1)}$$

$$\equiv\frac{\Phi}{\tau^2}\left[\frac{a}{Z}\right]^2\eta(q)\ , \tag{5.1}$$

where

$$\Phi\equiv[(1-\tau\alpha^2z^2/4)^2+(\alpha z)^2]^{-1}\ , \tag{5.2}$$

and

$$\tau\equiv\omega/(\alpha Z^2/2a) \tag{5.3}$$

is the photon energy measured in units of the ionization energy. From Eq. (5.1), we have

$$\mathrm{Im}P_{q+1}(\omega)=\left[\Phi\left[\frac{a^2}{Z^2\tau^2}\right]\right]^{q+1}\left[\prod_{j=0}^{q}\eta(j)\right]\mathrm{Im}P_0(\omega)\ . \tag{5.4}$$

From Eq. (3.18), we have

$$\mathrm{Im}Q_q(\omega)=2(q+1)\omega^2\mathrm{Im}P_{q+1},\quad q\geq0\ . \tag{5.5}$$

Together with Eq. (3.13), Eqs. (5.4) and (5.5) imply that all the spectral functions $\rho_{X,n}$ for photon-hydrogenic ion scattering are expressible in terms of $\mathrm{Im}P_0(\omega)$.

The analytic expression for the scattering amplitude obtained by Gavrila and Costescu[13] includes retardation correction. Compared to the nonretarded result, $\mathrm{Im}P_0$ can be expressed in the following form:

$$\mathrm{Im}P_0=\Phi^2\Omega(\tau)\mathrm{Im}P_{0,\mathrm{NR}}\ , \tag{5.6}$$

where

$$\Omega(\tau)=\exp\{-2[\chi_{\mathrm{R}}(\tau)-\chi_{\mathrm{NR}}(\tau)]/\sqrt{\tau-1}\}\ , \tag{5.7}$$

$$\chi_{\mathrm{R}}(\tau)=\tan^{-1}\frac{2\sqrt{\tau-1}}{2-\tau+\frac{1}{4}\tau^2(\alpha z)^2}\ , \tag{5.8a}$$

and

$$\chi_{\mathrm{NR}}(\tau)=\tan^{-1}\frac{2\sqrt{\tau-1}}{2-\tau}\ , \tag{5.8b}$$

the subscripts R and NR stand for retarded and nonretarded and τ is given by Eq. (5.3). In the nonretarded approximation, $\mathrm{Im}P_{0,\mathrm{NR}}$ can be written in terms of the electric dipole oscillator strengths[14]

$$\mathrm{Im}P_{0,\mathrm{NR}}(\omega)=\frac{\pi\alpha^2a}{2}\sum_j{}'\omega_{j0}f_{j0}\delta(\omega-\omega_{j0})\ , \tag{5.9}$$

where the prime over the summation sign indicates the inclusion of the continuum states and

$$f_{j0}=2m\omega_{j0}|\langle j|z|0\rangle|^2 \tag{5.10}$$

is the electric dipole oscillator strength, and

$$\omega_{j0}\equiv E_j-E_0=\frac{Z^2\alpha}{2a}(1-1/j^2) \tag{5.11}$$

is the resonant excitation energy to the jth level from the ground state. Equations (3.12), (3.13), (5.4)—(5.11) enable us to write the spectral functions $\rho_{X,n}$ in terms of the dipole oscillator strengths

$$\rho_{E,q}(\omega)=(1+q)\left[\frac{a}{\tau Z}\right]^{2q}\Phi^q\frac{1+(\alpha Z)^2\Phi\eta(q)/2}{1+(\alpha Z)^2\Phi\eta(0)/2}\times\left[\prod_{j=0}^{q-1}\eta(j)\right]\rho_{E,0}(\omega)\ , \tag{5.12}$$

$$\rho_{E,0}(\omega)=[1+(\alpha Z)^2\Phi\eta(0)/2]\Phi^2\Omega(\tau)\frac{2\pi^2\alpha^2a}{\omega^2}\times\sum_j{}'\omega_{j0}f_{j0}\delta(\omega-\omega_{j0})\ , \tag{5.13}$$

$$\rho^{\mathrm{dia}}_{M,q}(\omega)=-2\omega^2(q+1)\left[\frac{a}{\tau Z}\right]^{2q+2}\Phi^{q+1}\left[\prod_{j=0}^{q}\eta(j)\right]\times\rho_{E,0}(\omega)/[1+(\alpha Z)^2\Phi\eta(0)/2]\ . \tag{5.14}$$

Lastly, we would like to add that the product of $\eta(j)$'s displays some interesting structure of the O_4 symmetry:

$$\prod_{j=0}^{q}\eta(j)=\prod_{j=0}^{q}\frac{(2+j)^2(\tau-1)+1}{(j+5/2)(j+1)}=\frac{3(q+2)2^{2q+3}[(q+2)!]^2}{(2q+5)!\tau}\times\prod_{j=1}^{q+2}[\tau-(1-1/j^2)]\ . \tag{5.15}$$

This is because $\rho_{E,q}$ is chiefly due to the 2^{q+1}th-pole interaction and $\rho_{M,q}$ is chiefly due the 2^{q+2}th-pole interaction. Equation (5.15) then indicates that the intermediate

states with principal quantum number $n \leq q+1$ do not contribute to $\rho_{E,q}$ and similarly the intermediate states with quantum number $n \leq q+2$ do not contribute to $\rho_{M,q}$. Equation (4.11) together with Eqs. (5.12)—(5.14) enable us to express the retarded higher-multipole long-range interaction potential in high-Rydberg states in heliumlike ions in terms of hydrogenic dipole oscillator strengths.

VI. RETARDATION EFFECT IN THE ELECTRIC QUADRUPOLE AND DIAMAGNETIC DIPOLE INTERACTIONS IN He RYDBERG STATES

We are now ready to calculate the energy shifts in He Rydberg states due to the retarded electromagnetic multipole long-range interaction between the hydrogenic core ions and the outer Rydberg electron according to Eqs. (4.1) and (5.12)—(5.14). The major retardation correction to the energy levels arises in the electric dipole interaction and the results have been given by us previously.[8] As our calculation shows, the retardation correction is best understood by an examination of the low-argument expansions for the functions $J_E(\omega R)$ and $J_M(\omega R)$ used in Eq. (4.1):

$$J_E(\omega R)=8\left[\frac{3\pi}{2\omega R}-\frac{11}{4}+\frac{\pi}{2}\omega R+O(\omega^2R^2)\right], \quad (6.1)$$

$$J_M(\omega R)=8\left[\frac{5}{4}+\frac{\pi}{2}\omega R+O(\omega^2R^2)\right]. \quad (6.2)$$

If one substitutes the first term in this low-argument expansion of J_E, into Eq. (4.1), one recovers, for $n=0$, Drachman's[10] nonadiabatic β_1 term, and for $n=1$, his β_2 term. Higher values of n produce higher-multipole analogs of Drachman's nonadiabatic terms. The second term in the low-agreement expansion of J_E in Eq. (6.1) or the first term in the low-agreement expansion for J_M in Eq. (6.2), upon substitution in Eq. (4.1), exactly cancels the second term in the right-hand side of Eq. (4.1) depending on whether $X=E$ or M. That is, at small distances, there is no analog to the generalized multipole Kelsey-Spruch-Bernabau-Tarrach (KSBT) terms.[11,12] In view of the very precise calculations of the nonretarded energy shifts in He Rydberg states by Drachman,[10] we define the multipole retardation-correction potential in Eq. (4.1) by

$$V_{X,n}^{\rm corr}(R)=\frac{\alpha\lambda}{16\pi^2R}\frac{d^{2n}}{dR^{2n}}\int_0^\infty d\omega\frac{1}{\pi}\frac{\rho_{X,n}(\omega)}{\omega R^4}J_X^{\rm corr}(\omega R), \quad (6.3)$$

where

$$J_E^{\rm corr}(\omega R)\equiv J_E(\omega R)-\frac{12\pi}{\omega R}+22 \quad (6.4)$$

$$=4\pi\omega R+O(\omega^2R^2) \quad (6.4a)$$

and

$$J_M^{\rm corr}(\omega R)\equiv J_M(\omega R)+20 \quad (6.5)$$

$$=4\pi\omega R+O(\omega^2R^2). \quad (6.5a)$$

The results for $X=E$ and $n=0$, i.e., the electric dipole retardation correction to the potential and its expectation values, in various Rydberg states in He and He-like ions of high Z have been given in detail.[8] According to this calculation, the electric dipole retardation correction is accounted for, within a factor of 2, by just taking the leading term in the low-agreement expansion of $J_E^{\rm corr}(\omega R)$. We might wish to point out that the terms in this expansion appear with opposite signs. When dealing with the retardation effect for the electric quadrupole and the diamagnetic dipole interactions, it seems pointless at present to require an accuracy beyond a factor of 2 since there are other effects due to recoil and relativistic corrections that are comparable in size but which have not been properly accounted for. Hence we content ourselves with just keeping the leading terms (in the following denoted by "lead. corr") in the low-agreement expansions for J_E and J_M in Eqs. (6.4a) and (6.5a) when used in obtaining the retardation-correction potential in Eq. (6.3). We then obtain

$$V_{E,1}^{\rm lead.\ corr}(R)=\frac{\alpha\lambda}{16\pi^2R}\frac{d^2}{dR^2}\int_0^\infty d\omega\frac{4}{R^3}\rho_{E,1}(\omega), \quad (6.6)$$

and

$$V_{M,0}^{\rm lead.\ corr}(R)=\frac{\alpha\lambda}{16\pi^2R}\int_0^\infty d\omega\frac{4}{R^3}\rho_{M,0}(\omega). \quad (6.7)$$

We can now use the results in Eqs. (5.12)—(5.14) in the last section in the final approximation

$$\rho_{E,1}(\omega)\sim\rho_{E,1}^{\rm lead.}(\omega)=\frac{(Z\alpha)^2}{5\omega^2}\left[\frac{8\omega a}{Z^2\alpha}-3\right]\frac{2\pi^2\alpha^2a}{\omega^2}\times\sum_j{}'\omega_{j0}f_{j0}\delta(\omega-\omega_{j0}), \quad (6.8)$$

and

$$\rho_{M,0}(\omega)\sim\rho_{M,0}^{\rm lead.}=-\omega^2\rho_{E,1}^{\rm lead.} \quad (6.9)$$

where by "lead.," we mean we have neglected terms of order $(Z\alpha)^2$ compared to 1. With the approximations expressed in Eqs. (6.8) and (6.9), Eqs. (6.6) and (6.7) can be evaluated in closed forms:

$$V_{E,1}^{\rm lead.\ corr}(R)=9\frac{\alpha^3}{Z^4}\frac{a^5}{R^6}, \quad (6.10)$$

and

$$V_{M,0}^{\rm lead.\,corr}(R)=-\frac{\alpha^5}{5}\frac{a^3}{R^4}. \quad (6.11)$$

We note that Eq. (6.11) is Z independent and is of order $(Z\alpha)^2$ smaller than the leading electric dipole retardation correction [the leading term in Eq. (10) of Ref. 8]. Together with our earlier observation that there is a cancellation with the magnetic multipole analog of the KSBT term, it seems that diamagnetic effects in the Rydberg states are quite negligible. This is, however, not quite so for the electric quadrupole retardation effect since this is of order $(Z\alpha)^2$ compared to Drachman's nonadiabatic electric dipole term (his β_1 term). In Table I, we give the expectation values of $V_{E,1}^{\rm lead.\ corr}(R)$ and $V_{M,0}^{\rm lead.\ corr}(R)$ for the $n=10$, $l=4$—9 He Rydberg states. For comparison purpose we also reproduce the corresponding expectation

TABLE I. Expectation values in cps of the leading electric quadrupole retardation correction $\langle V_{E,1}^{\text{corr}'} \rangle$, the leading diamagnetic dipole correction $\langle V_{M,0}^{\text{corr}'} \rangle$, and the electric dipole retardation correction $\langle V_{E,0}^{\text{corr}} \rangle$ in $n=10$ Rydberg states of neutral helium. The expectation values of the leading approximation to the electric dipole retardation correction $\langle V_{E,0}^{\text{corr}'} \rangle$ is also given for comparison. The numbers in parentheses indicate powers of 10 to be multiplied.

l	$\langle V_{E,1}^{\text{corr}'} \rangle$	$\langle V_{M,0}^{\text{corr}'} \rangle$	$\langle V_{E,0}^{\text{corr}} \rangle$	$\langle V_{E,0}^{\text{corr}'} \rangle$
4	1.42(3)	−3.02(0)	6.18(4)	7.08(4)
5	1.84(2)	−1.04(0)	2.02(4)	2.45(4)
6	3.31(1)	−4.27(−1)	7.73(3)	1.00(4)
7	7.28(0)	−1.96(−1)	3.28(3)	4.61(3)
8	1.79(0)	−9.76(−2)	1.49(3)	2.29(3)
9	4.52(−1)	−5.13(−2)	6.99(2)	1.21(3)

values of the electric dipole retardation-correction potential for the same states given in Ref. 8.

CONCLUDING REMARKS

We have considered the elastic scattering of photons by a spinless neutral atom in the special case where both the orbital angular momentum and the total spin (nuclear and electronic) is zero. From rotational invariance, in the rest frame of the heavy atom, the scattering amplitude necessarily have the form $A(\omega,\theta)(\boldsymbol{\epsilon}\cdot\boldsymbol{\epsilon}')+B(\omega,\theta)(\boldsymbol{\epsilon}\cdot\mathbf{k}')(\boldsymbol{\epsilon}'\cdot\mathbf{k})$ where $(\boldsymbol{\epsilon},\mathbf{k})$ and $(\boldsymbol{\epsilon}',\mathbf{k}')$ are the polarization and momentum vectors of the incident and scattered photons, and $\omega=|\mathbf{k}|=|\mathbf{k}'|$ is the photon energy and θ is the scattering angle. The amplitudes A and B are related to the electric and magnetic form factors. To the extent that we neglect hyperfine splitting compared to atomic-level splitting, we show that inclusion of the Pauli spin interaction with the photon field leads only to a magnetic form factor even though retardation is included. When the radiation Hamiltonian is given by the minimal-coupling scheme, the seagull interaction ($\sim A^2$) contributes only to the real part of the electric form factor. In the dipole approximation, the $\mathbf{p}\cdot\mathbf{A}$ interaction leads only to the electric form factor but contributes to both the real and imaginary parts. However, when retardation is included, the $\mathbf{p}\cdot\mathbf{A}$ interaction leads to both the electric and magnetic form factors. For scattering by atoms in the ground state, only the direct graph gives rise to an imaginary part in these form factors. When expressed as a power series in $\cos\theta$ or in t where t is the invariant 4-momentum transfer square, the electric and magnetic form factors are related in a simple way. This relation is a consequence of the rotational invariance of the atomic state and does not rely on the details of the atomic structure.

We have thus shown that in elastic photon scattering by atoms in the S state, when spin interaction is neglected, the electric and magnetic form factors are not independent. On setting $\mathrm{Im}F_X(\omega,t)=\rho_X(\omega,t)=\sum_{n=0}^{\infty}\rho_{X,n}(\omega)t^n$, where $X=E$ or M, we find that the independent spectral functions are $\rho_{E,0}$ and $\rho_{M,n}$'s, or equivalently all $\rho_{E,n}$'s. Previously, it has been shown that the higher-multipole contribution to the retarded long-range interaction between a pair of spinless atoms and between a spinless atom and a point-charge particle is expressible in terms of the $\rho_{X,n}$'s. In view of the dependence among the electric and magnetic spectral functions discussed here, we reexamine the higher-multipole contribution to the retarded long-range interaction potential in high-Rydberg states in heliumlike ions where sufficient advances in experimental techniques have given hopes to the observability of these retardation effects. We have estimated the relative contribution of various multipoles to the total potential. In the special case of Rydberg states in heliumlike ions, there exists an additional relation among the successive $\rho_{X,n}$'s because of the O_4 symmetry in hydrogen since the core of the heliumlike Rydberg ion is a hydrogenic ion. We find then all the multipole contributions to the retarded van der Waals potential are expressible in terms of the hydrogenic dipole oscillator strengths. We have estimated the order of the retardation correction to the He Rydberg state ($n=10$) energy levels due to the electric quadrupole and diamagnetic dipole interactions. These amount to about 1% of the correction due to retardation effects in the leading electric dipole interaction. We have refrained from giving a more detailed calculation of the retarded multipole interaction effects because there are corrections of comparable order due to recoil and relativistic effects which are not addressed in the present paper. We hope to return to discuss this in the future.

ACKNOWLEDGMENTS

This work is supported in part by the National Science Foundation EPSCOR under Grant No. ISP-80-11451 and in part by the University of South Carolina. Part of this work was performed while I was a participant in the Lewes Centre for Physics. I thank the center for hospitality and would like to express my indebtedness to Professor Gerald Feinberg who, in a somewhat related work 14 years ago, introduced me to the pleasure of theoretical physics and through recent collaboration revives my interest in the present problem. I also thank Professor Yakir Aharonov for helpful discussions.

*Permanent address.

[1]H. B. G. Casimir and D. Polder, Phys. Rev. **73**, 360 (1948).
[2]F. London, Z. Phys. **63**, 245 (1930).
[3]G. Feinberg and J. Sucher, Phys. Rev. A **2**, 2395 (1970).
[4]C. K. Au and G. Feinberg, Phys. Rev. A **6**, 2433 (1972).
[5]G. Feinberg, Phys. Rev. B **9**, 2490 (1974).
[6]S. L. Palfrey and S. R. Lundeen, Phys. Rev. Lett. **53**, 1141 (1984).
[7]G. Feinberg and J. Sucher, Phys. Rev. A **27**, 1958 (1983).
[8]C. K. Au, G. Feinberg, and J. Sucher, Phys. Rev. Lett. **53**, 1145 (1984).
[9]C. K. Au, J. Phys. B **11**, 2871 (1978).

[10]R. J. Drachman, Phys. Rev. A **26**, 1228 (1982).
[11]E. J. Kelsey and L. Spruch, Phys. Rev. A **18**, 1055 (1978); **18**, 845 (1978); **18**, 15 (1978).
[12]J. Bernabeu and R. Tarrach, Ann. Phys. (N.Y.) **102**, 323 (1976).
[13]M. Gavrila and A. Costescu, Phys. Rev. A **2**, 1752 (1970).
[14]C. K. Au, Phys. Rev. A **6**, 1232 (1972).