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Some applications of excited-state–excited-state transition densities[*]

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We derive an approximation for transition moments between excited states consistent with the approximations and assumptions normally used to obtain transition moments betwen the ground and excited states in the random-phase approximation and its higher-order approximations. We apply the result to the calculation of the photoionization cross sections of the $2\,^3S$ and $2\,^1S$ metastable states of helium by a numerical analytical continuation of the frequency-dependent polarizability. The procedure completely avoids the need for continuum basis functions. The cross sections agree well with the results of other calculations. We also predict an accurate two-photon decay rate for the $2\,^1S$ metastable state of helium. The entire procedure is immediately applicable to several problems involving photoionization of metastable states of molecules.

I. INTRODUCTION

In the equations-of-motion method or any of its approximations, e.g., the random-phase approximation or time-dependent Hartree-Fock, the quantities calculated directly are the transition densities between the ground and excited states.[1] Relative quantities between the ground and excited states such as transition moments can then be readily obtained from these transition densities and the necessary matrix elements between basis states. For several applications excited-state–excited-state transition densities are needed. These include the study of transition intensities between excited states of molecules of interest in the development of gas-phase lasers, e.g., the $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$ lasing transition in N_2, and in atmospheric emissions where transitions between excited states play an important role. Other properties such as two-photon decay of metastable states and the polarizabilities of excited states require infinite summations over excited-state–excited-state transition moments and frequencies.

The purpose of this paper is to show how excited-state–excited-state transition moments can be calculated directly from the set of ground-state–excited-state transition densities obtained from a single equations-of-motion calculation. First, we derive the simple relationship expressing the excited-state–excited-state transition moment directly in terms of the ground-state–excited-state transition densities. Then we discuss two interesting applications of this result. The first application is to the calculation of the photoionization cross sections of the $2\,^3S$ and $2\,^1S$ metastable states of helium. In this calculation of photoionization cross sections we completely avoid the need for constructing continuum solutions of the wave equation normally needed to describe the final-state continuum wave functions. The central idea is to use the excited-state–excited-state transition moments to obtain a discrete representation of the frequency-dependent polarizability at complex values of the energy. Numerical analytic continuation can then be used to obtain the photoionization cross sections. We have previously applied this procedure to obtain photoionization cross sections for He and H_2 ground states in good agreement with experiment.[2,3] As a second application, we use these excited state moments to predict the two-photon decay rate of the $2\,^1S$ metastable state of helium. Both the calculated photoionization cross sections of the $2\,^1S$ and $2\,^3S$ states of helium and the two-photon decay rate of the $2\,^1S$ state agree well with the results of other calculations and available experimental data.

II. THEORY

In the study of dynamical properties of atoms and molecules the quantities of direct physical interest are relative quantities between two states, e.g., excitation frequencies $\omega_{0\lambda}$ and transition matrix elements $\langle 0|M|\lambda\rangle$ between states $|0\rangle$ and $|\lambda\rangle$. For example, in the frequency-dependent polarizability $\alpha(\omega)$

$$\alpha(\omega) = \mathop{\mathrm{S}}\limits_{\lambda_i \neq 0} \frac{2\omega_{0\lambda_i} |\langle 0|\vec{\mathrm{D}}|\lambda_i\rangle|^2}{\omega_{0\lambda_i}^2 - \omega^2}, \tag{1}$$

one is concerned with a set of frequencies $\{\omega_{0\lambda}\}$ and the off-diagonal matrix elements of the dipole operator $\vec{\mathrm{D}}$. The summation in Eq. (1) implies an integration over the continuum. The evaluation of one-particle transition matrix elements simply requires a knowledge of the one-particle transition density $\rho_{0\lambda}(\vec{r}', \vec{r})$,

$$\rho_{0\lambda}(\vec{r}', \vec{r}) = \langle 0|\rho(\vec{r}', \vec{r})|\lambda\rangle, \tag{2}$$

where $\rho(\vec{r}', \vec{r})$ is the one-particle density operator

$$\rho(\vec{r}', \vec{r}) = \hat{\psi}^\dagger(\vec{r}')\hat{\psi}(\vec{r}) \tag{3}$$

in second quantized form with $\hat{\psi}^\dagger(\vec{r})$ and $\hat{\psi}(\vec{r})$ the field operators, e.g.,

$$\hat{\psi}^\dagger(r) = \sum_k \phi_k^*(r) a_k^\dagger , \tag{4}$$

where $\phi_k(r)$ and $a_k^\dagger$ are single-particle states and creation operators, respectively. The transition matrix element of a one-particle operator M can then be written

$$\langle 0|M|\lambda\rangle = \int d\vec{r}d\vec{r}'\delta(\vec{r} - \vec{r}')M(r)\rho_{0\lambda}(\vec{r}', \vec{r}) , \tag{5}$$

where the integration over the δ function is performed after $M(r)$ is applied. Since the one-particle transition density is sufficient to evaluate the physically significant matrix elements, one should design a theory that concentrates directly on this quantity. In the equations-of-motion method as well as in several other many-body methods, e.g., in the theory of Green's function, we calculate the transition density directly.

In the equations-of-motion method one calculates the elements of the ground-state–excited-state transition densities by solving the equation of motion of the excitation operator $O_\lambda^\dagger$ defined such that $O_\lambda^\dagger|0\rangle = |\lambda\rangle$. It can be shown that if the operator $O_\lambda^\dagger$ is restricted to single particle-hole form, i.e.,

$$O_\lambda^\dagger = \sum_{m\gamma} [Y_{m\gamma}(\lambda)a_m^\dagger a_\gamma - Z_{m\gamma}(\lambda)a_\gamma^\dagger a_m] ; \tag{6}$$

the amplitudes $Y_{m\gamma}(\lambda)$ and $Z_{m\gamma}(\lambda)$ satisfy the equation[4]

$$\begin{pmatrix} \underline{A} & \underline{B} \\ -\underline{B}^* & -\underline{A}^* \end{pmatrix} \begin{pmatrix} \underline{Y}(\lambda) \\ \underline{Z}(\lambda) \end{pmatrix} = \omega_{0\lambda} \begin{pmatrix} \underline{D} & 0 \\ 0 & \underline{D} \end{pmatrix} \begin{pmatrix} \underline{Y}(\lambda) \\ \underline{Z}(\lambda) \end{pmatrix} . \tag{7}$$

The matrices $\underline{A}$, $\underline{B}$, and $\underline{D}$ are ground-state expectation values of second-quantized operators[1] and $\omega_{0\lambda}$ the excitation energy. The amplitudes $Y_{m\gamma}$ and $Z_{m\gamma}$ are elements of the transition density, which, to a good approximation, can be written

$$\begin{aligned} \rho_{0\lambda}(\vec{r}', \vec{r}) &= \langle 0|[\rho, O_\lambda^\dagger]|0\rangle \\ &\approx \sum_{m\gamma} [Y_{m\gamma}\phi_m^*(\vec{r}')\phi_\gamma(\vec{r}) + Z_{m\gamma}\phi_\gamma^*(\vec{r}')\phi_m(\vec{r})] , \end{aligned} \tag{8}$$

where ϕ_m and ϕ_γ are particle and hole states, respectively. The equations of motion, Eq. (7), can be solved straightforwardly in various approximations for ground-to-excited-state transition energies and densities. Applications to several molecules, e.g., H_2, N_2, CO, H_2O, CO_2, H_2CO, and C_6H_6,[5] show that the method yields accurate dipole transition moments.

For several applications it would be convenient to derive excited-state–excited-state transition moments directly from the set of ground-state–excited-state transition densities $\{\rho_{0\lambda}\}$ obtained from the solution of Eq. (7). Consider the matrix element of the one-body operator between states $|\lambda_i\rangle$ and $|\lambda_j\rangle$. From the properties of the operators $O_{\lambda_i}^\dagger$ and $O_{\lambda_j}^\dagger$ we can write

$$\langle\lambda_i|M|\lambda_j\rangle = \langle 0|O_{\lambda_i}MO_{\lambda_j}^\dagger|0\rangle . \tag{9}$$

We now exploit the formal properties of the excitation operators to rewrite Eq. (9) as the expectation value of commutators of the operators O_{λ_i}, M, and $O_{\lambda_j}^\dagger$,

$$\begin{aligned} \langle\lambda_i|M|\lambda_j\rangle = &\langle 0|[O_{\lambda_i}, M, O_{\lambda_j}^\dagger]|0\rangle \\ &+ \tfrac{1}{2}\langle 0|[O_{\lambda_i}, O_{\lambda_j}^\dagger]T|0\rangle \\ &+ \tfrac{1}{2}\langle 0|T[O_{\lambda_i}, O_{\lambda_j}^\dagger]|0\rangle , \end{aligned} \tag{10}$$

where the double commutator is defined as

$$2[O_{\lambda_i}, M, O_{\lambda_j}^\dagger] = [[O_{\lambda_i}, M], O_{\lambda_j}^\dagger] + [O_{\lambda_i}, [M, O_{\lambda_j}^\dagger]] . \tag{11}$$

The advantage in going from the expectation value of the direct product of operators O_{λ_i}, M, $O_{\lambda_j}^\dagger$ of Eq. (9) to the expectation value of the double commutator of these operators, Eq. (11), is due to the observation that the double commutator is a simpler operator, i.e., of lower particle-hole rank, than the straightforward product.[6] The expectation value of the double commutator can then be expected to be less sensitive to the details of the ground-state wave function.[4]

The right-hand side of Eq. (10) is now evaluated in three different approximations. First in the random-phase approximation (RPA) the second and third terms of Eq. (10) vanish since $[O_{\lambda_i}, O_{\lambda_j}^\dagger] = \delta_{\lambda_i\lambda_j}$, $|\lambda_i\rangle \neq |\lambda_j\rangle$, and the expectation value of the double commutator is evaluated over the Hartree-Fock (HF) ground state. In the RPA we obtain

$$\begin{aligned} \langle\lambda_i|M|\lambda_j\rangle \approx \sum_{n\nu}\sum_{m\gamma} &[Y_{n\nu}^*(\lambda_i)Y_{m\gamma}(\lambda_j) + Z_{n\nu}^*(\lambda_i)Z_{m\gamma}(\lambda_j)] \\ &\times [T_{nm}\delta_{\nu\gamma} - T_{\gamma\nu}\delta_{nm}] . \end{aligned} \tag{12}$$

In Eq. (12) m and n denote particle states and γ and ν hole states. The amplitudes $\{Z_{n\nu}\}$ implicitly account for electron correlation in the ground state. The $\{Y_{n\nu}\}$ amplitudes are the dominant effect in Eq. (12) since they represent the main correlation effects in the excited state. If we completely neglect electron correlation in the ground state, i.e., set $|0\rangle = |\mathrm{HF}\rangle$ and $\{Z_{n\nu}\} = 0$, we obtain

$$\begin{aligned} \langle\lambda_i|M|\lambda_j\rangle \approx \sum_{n\nu}\sum_{m\gamma} &Y_{n\nu}^*(\lambda_i)Y_{m\gamma}(\lambda_j) \\ &\times [T_{nm}\delta_{\nu\gamma} - T_{\gamma\nu}\delta_{nm}] . \end{aligned} \tag{13}$$

This corresponds to assuming that the excited state is composed of single excited states relative to the HF ground state, i.e., single excitation configuration interaction or the Tamm-Dancoff approximation (TDA). Equation (13) should normally be a good approximation to the transition matrix element.

The third approximation to $\langle\lambda_i|M|\lambda_j\rangle$ can be obtained by solving Eq. (7) for the $\{Y_{n\nu}\}$ and $\{Z_{n\nu}\}$ amplitudes in a higher-order scheme. This higher random-phase approximation is discussed in Ref. 1 and is often needed in discussing excitations to low-lying triplet electronic states where the RPA may show instabilities. In this approximation (HRPA) we have

$$\langle\lambda_i|M|\lambda_j\rangle \approx \sum_{n\nu}\sum_{m\gamma}[Y^*_{n\nu}(\lambda_i)Y_{m\gamma}(\lambda_j)+Z^*_{n\nu}(\lambda_i)Z_{m\gamma}(\lambda_j)]$$

$$\times\left[T_{\gamma\nu}\rho_{nm}+T_{nm}\rho_{\nu\gamma}-\tfrac{1}{2}\delta_{\nu\gamma}\left(\sum_{p}T_{mp}\rho_{pn}+T_{np}\rho_{pm}\right)-\tfrac{1}{2}\delta_{nm}\sum_{\delta}(T_{\nu\delta}\rho_{\delta\gamma}+T_{\gamma\delta}\rho_{\delta\nu})\right], \tag{14}$$

where ρ is the ground-state density matrix, γ, δ, and ν hole states, and m, n, and p particle states. In the HRPA the second and third terms of Eq. (10) do not exactly vanish but can be expected to be small and are neglected in deriving Eq. (14). We recall that these terms do vanish in the RPA since $[O_{\lambda_i}, O^\dagger_{\lambda_j}]=\delta_{\lambda_i\lambda_j}$. There are examples where it is important to use Eq. (14) instead of Eq. (12) or Eq. (13), e.g., in certain transitions in N_2. These results will be discussed in a separate paper.[7]

In Sec. III we discuss the applications of these transition moments to the calculation of photoionization cross sections of the $2\,^1S$ and $2\,^3S$ metastable states of helium and of the two-photon decay rate of the $2\,^1S$ state of helium.

III. APPLICATIONS

A. Photoionization cross sections of metastable states

Photoionization of excited-state species plays an important role in several physical systems. For example, photoionization of rare-gas excimers is an important reaction that may limit the laser gain of these systems. In previous calculations of photoionization cross sections of metastable states,[8,9] as well as for ground states, accurate atomic or molecular continuum eigenfunctions are needed to describe the final states of the systems.[10] We have recently shown how one can completely avoid the need for continuum eigenfunctions in the calculation of atomic and molecular photoionization cross sections.[11,12] These calculated photoionization cross sections for He [11] and H_2 [12] in their ground states agree well with other calculations and experiment. The central idea is to obtain a discrete representation of the frequency-dependent polarizability, which, although not directly useful at physical energies in the continuum, often provides an adequate representation of the polarizability for complex values of the energy. Numerical analytic continuation can then be used to return to the real energy axis where the physical information is desired. This L^2 method for calculating photoionization cross sections was suggested by Broad and Reinhardt,[13] who applied it to atomic hydrogen.

To apply this method to the calculation of photoionization cross sections of excited states we start from the frequency-dependent polarizability of the excited state. For the state $|\lambda_i\rangle$ we have

$$\alpha_{\lambda_i}(z)=\sum_{\lambda_i\neq\lambda_j}\frac{f_{\lambda_i\lambda_j}}{\omega^2_{\lambda_i\lambda_j}-z^2}+\int_{\epsilon_I}^{\infty}\frac{g_{\lambda_i}(\epsilon)d\epsilon}{\epsilon^2-z^2}, \tag{15}$$

where z is complex and $\omega_{\lambda_i\lambda_j}$, $f_{\lambda_i\lambda_j}$, and $g_{\lambda_i}(\epsilon)$ are the transition frequencies and the bound and continuum oscillator strengths, respectively, and ϵ_I is the first ionization threshold of the system. In the neighborhood of $z=\omega+i\eta$ with $\eta\to 0$

$$\alpha_{\lambda_i}(\omega)=\sum_{\lambda_i\neq\lambda_j}\frac{f_{\lambda_i\lambda_j}}{\omega^2_{\lambda_i\lambda_j}-\omega^2}+\mathrm{P}\int_{\epsilon_I}^{\infty}\frac{g_{\lambda_i}(\epsilon)d\epsilon}{\epsilon^2-\omega^2}+i\pi\frac{g_{\lambda_i}(\omega)}{2\omega}. \tag{16}$$

This gives the relation between the photoionization cross sections of state $|\lambda_i\rangle$, σ_{λ_i}, and the imaginary part of its polarizability

$$\sigma_{\lambda_i}(\omega)=\lim_{\eta\to 0}(4\pi\omega/c)\,\mathrm{Im}[\alpha_{\lambda_i}(\omega+i\eta)]. \tag{17}$$

$\alpha(z)$ of Eq. (15) is first approximated by a finite sum over approximate oscillator strengths $\tilde{f}_{\lambda_i\lambda_j}$ and frequencies $\tilde{\omega}_{\lambda_i\lambda_j}$,

$$\tilde{\alpha}_{\lambda_i}(z)=\sum_{\lambda_i\neq\lambda_j}\frac{\tilde{f}_{\lambda_i\lambda_j}}{\tilde{\omega}^2_{\lambda_i\lambda_j}-z^2}. \tag{18}$$

To continue $\alpha_{\lambda_i}(z)$ analytically on to the real axis, we construct a low-order rational-fraction representation of $\alpha_{\lambda_i}(z)$ by fitting it to the approximate $\tilde{\alpha}_{\lambda_i}(z)$ of Eq. (18) at a number of points in the complex plane.[14] With this smooth representation of $\tilde{\alpha}_{\lambda_i}(z)$ we can now calculate $\alpha_{\lambda_i}(z)$, and hence $\sigma_{\lambda_i}(z)$, at real energies where the original discrete approximation, Eq. (18), is unphysical.

The finite set of oscillator strengths $\tilde{f}_{\lambda_i\lambda_j}$ and

TABLE I. RPA transition moments and oscillator strengths for the $2\,^1S\to\lambda\,^1P$ and $2\,^3S\to\lambda\,^3P$ transitions used to evaluate $\tilde{\alpha}_{\lambda_i}(z)$, Eq. (18).[a]

$2\,^1S\to$	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$	$6\,^1P$	$7\,^1P$	$8\,^1P$	$9\,^1P$
$\lvert M\rvert$[b]	3.021	0.9047	0.5945	0.6430	0.4793	0.1646	0.0296	0.0036
f[b]	0.3917	0.1442	0.0815	0.1334	0.1428	0.0480	0.0060	0.0003
$2\,^3S\to$	$2\,^3P$	$3\,^3P$	$4\,^3P$	$5\,^3P$	$6\,^3P$	$7\,^3P$	$8\,^3P$	$9\,^3P$
$\lvert M\rvert$	2.330	0.3884	0.2971	0.4208	0.4971	0.3310	0.0922	0.0098
f	0.6094	0.0407	0.0289	0.0723	0.1634	0.1806	0.0552	0.0025

[a] $f_{\lambda_i\lambda_j}=2\omega_{\lambda_i\lambda_j}|M|^2$ for $S\to P$ transitions.
[b] In atomic units.

transition frequencies $\tilde{\omega}_{\lambda_i\lambda_j}$ needed to obtain $\tilde{\alpha}_{\lambda_i\lambda_j}$, Eq. (18), is generated by solving the equations of motion, Eq. (7), for the transition frequencies $\omega_{0\lambda}$. The resulting transition amplitudes $Y_{n\nu}$ and $Z_{n\nu}$ give, through Eqs. (12), (13), or (14), the excited-state–excited-state transition moments $\tilde{M}_{\lambda_i\lambda_j}$, which, along with $\tilde{\omega}_{\lambda_i\lambda_j}$, define $\tilde{f}_{\lambda_i\lambda_j}$,

$$\tilde{f}_{\lambda_i\lambda_j}=\tfrac{2}{3}\tilde{\omega}_{\lambda_i\lambda_j}|\langle\lambda_i|\vec{D}|\lambda_j\rangle|^2 . \qquad (19)$$

$\vec{D}$ is the dipole moment operator and the transition moment $D_{\lambda_i\lambda_j}$ is evaluated in the three approximations discussed above, i.e., Eqs. (12)–(14). In the calculation of the photoionization cross sections of the $2\,^1S$ and $2\,^3S$ metastable states of helium we use a finite set of eight discrete oscillator strengths, i.e., $f_{\lambda_i\lambda_j}(2\,^{1,3}S\to n\,^{1,3}P)$, $n=2, 3,\ldots 9$, in Eq. (18). Table I lists these oscillator strengths in the RPA which are used in the calculation of the photoionization cross sections. We do not list the oscillator strengths in the other approximations for all eight transitions since all the approximations can be expected to give similar results where excited-state correlation effects are not critical, e.g., in the $1s2s(2\,^1S)\to 1s2p(2\,^1P)$ transition the main effect is included in the TDA. In Table II we do, however, show the first three oscillator strengths and compare them with the results of other calculations.

TABLE II. Transition moments and oscillator strengths for the $2\,^1S\to\lambda\,^1P$ and $2\,^3S\to\lambda\,^3P$ transitions in different approximations.

$2\,^1S\to$		$2\,^1P$	$3\,^1P$	$4\,^1P$
TDA[a]	$\lvert M\rvert$	3.035	0.9255	0.6053
	f	0.3824	0.1494	0.0839
RPA[a]	$\lvert M\rvert$	3.021	0.9047	0.5945
	f	0.3917	0.1442	0.0815
HRPA[a]	$\lvert M\rvert$	3.012	0.9285	0.5985
	f	0.3766	0.1526	0.0831
Weiss[b]	$\lvert M\rvert$	2.916	0.9020	0.4699
	f	0.3764	0.1478	0.0508
Schiff[c]	$\lvert M\rvert$	2.916	0.9129	
	f	0.3764	0.1514	
$2\,^3S\to$		$2\,^3P$	$3\,^3P$	$4\,^3P$
TDA	$\lvert M\rvert$	2.364	0.4283	0.3194
	f	0.5857	0.0480	0.0325
RPA	$\lvert M\rvert$	2.330	0.3884	0.2971
	f	0.6094	0.0407	0.0289
HRPA	$\lvert M\rvert$	2.341	0.4319	0.3168
	f	0.5819	0.0497	0.0326
Weiss	$\lvert M\rvert$	2.531	0.5230	0.2896
	f	0.5391	0.0641	0.0240
Schiff	$\lvert M\rvert$	2.5314	0.5247	
	f	0.5391	0.0645	

[a] See text.
[b] A. W. Weiss, J. Res. Natl. Bur. Stand. (U. S.) A 71, 163 (1967).
[c] B. Schiff and C. L. Pekeris, Phys. Rev. 134, A638 (1964).

Figures 1 and 2 show the calculated photoionization cross sections for the $2\,^1S$ and $2\,^3S$ metastable states of helium. These cross sections are for the continuous background photoionization below the $n=2$ threshold. The fitting points for determining the rational-fraction representation of $\tilde{\alpha}_{\lambda_i}(z)$ were

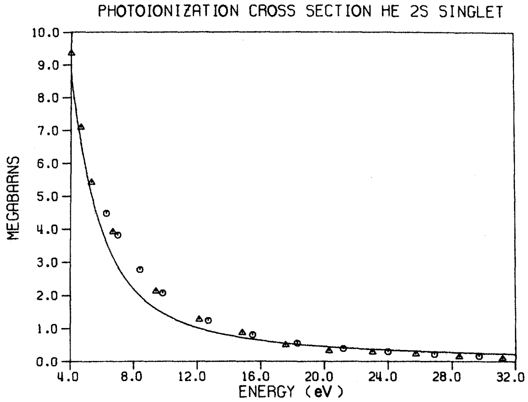

FIG. 1. Photoionization cross sections of the $2\,^1S$ state of helium in Mb. The curve shows the present cross sections obtained by numerical analytic continuation. The triangles and octagons are the calculated results of Norcross (Ref. 8) and Jacobs (Ref. 9), respectively.

chosen with a real part between each pair of $\omega^2_{\lambda_i\lambda_j}$ values of Table I, and the imaginary parts were varied over a region of the complex plane. For the different choices of the fitting points the calculated cross sections agree within (2–8)% of one another. In Figs. 1 and 2 we also plot the cross sections obtained by Norcross[8] and Jacobs,[9] who used Hartree-Fock and correlated initial-state wave functions, respectively, and close-coupling final-state wave functions. The agreement between these results and the present calculation is good. Within the experimental uncertainty of $\mp 14\%$, the various calculations agree well with the measured values.[15] The accuracy of our calculated cross sections could be improved by using a discrete set of $f_{\lambda_i\lambda_j}$'s and $\omega_{\lambda_i\lambda_j}$'s specifically designed to give photoionization cross sections of these metastable states. The f values used in this calculation were obtained from a calculation originally designed to give ground–excited-state energies and transition moments.

Finally, it should be emphasized that since this method completely avoids the use of continuum eigenfunctions, the techniques used here can be easily extended to molecules.[16] Some immediate applications would be the study of photoionization of excited states of rare-gas dimers and other molecular-gas lasers. For example, photoionization of the $A^1\Sigma_u^+$ state is critical in determining the possible gain of the proposed He_2 ultraviolet laser. These calculations can also provide estimates of the stimulated emission cross section, another important parameter in these laser systems.

B. Two-photon decay of the $2\,^1S$ metastable state

As a second application, and more in the purpose of a check on the discrete oscillator strength distribution of Table I, we now calculate the probability of two-photon decay of helium in the $2\,^1S$ level, i.e.,

$$\mathrm{He}(2\,^1S) \rightarrow \mathrm{He}(1\,^1S) + \hbar\omega_1 + \hbar\omega_2 . \qquad (20)$$

Accurate estimates, including those of a coupled Hartree-Fock calculation[17] and variational procedures,[18] have been obtained for this decay rate, and hence this application can serve as a useful calibration of our discrete f distribution.

Since the theory of two-quantum processes has been discussed elsewhere,[17, 18] our discussion of the basic equations will be brief. The probability of two-photon transitions can be formally expressed as an infinite summation over intermediate states. If $\hbar\omega_{0f}$ is the energy of the two-photon $\mathrm{He}(2\,^1S) \rightarrow \mathrm{He}(1\,^1S)$ transition of Eq. (20), the probability $A(y)\,dy$ that a photon will be emitted in the frequency range $\omega_{0f}\,dy$ is given by

$$A(y) = 5.299 \times 10^3 \omega_{0f}^5 y^3 (1-y)^3 |M(y)|^2 , \qquad (21)$$

where $y = \omega_1/\omega_{0f}$, and $M(y)$ is the two-photon transition matrix element

$$M(y) = \sum_{\lambda} \langle 2\,^1S|D_z|\lambda\,^1P\rangle \langle \lambda\,^1P|D_z|1\,^1S\rangle \times \left(\frac{\omega_{0f}}{\omega_{0\lambda} + y\omega_{0f}} + \frac{\omega_{0f}}{\omega_{0\lambda} + (1-y)\omega_{0f}} \right), \qquad (22)$$

where D_z is the z component of the dipole moment operator. The summation in Eq. (22) requires the transition moments between the ground and intermediate states, $\langle \lambda\,^1P|D|1\,^1S\rangle$, and between the metastable and intermediate states $\langle 2\,^1S|D|\lambda\,^1P\rangle$. The ground–excited-state transition moments are directly available from the solution of Eq. (7) in any approximation, e.g., the RPA or time-dependent Hartree-Fock approximation, and the excited-state–metastable-state transition moments can be derived in any of the approximations discussed in Eqs. (12), (13), or (14). Direct substitution of these moments and the corresponding energy differences yield estimates of the probability distribution $A(y)$. The Einstein A coefficient for two-photon emission is just the integral

$$A = \tfrac{1}{2} \int_0^1 A(y)\,dy . \qquad (23)$$

In Table III we list the values of $A(y)$ obtained using the RPA transition moments and frequencies throughout Eq. (22). It is important to note that for excited-state–excited-state transition moments we define the RPA as our approximation of Eq. (12) to the exact expression, Eq. (10). The agreement with the coupled Hartree-Fock calculations[17] and variational calculations[18] is good, but the results are generally about 10% too high. This

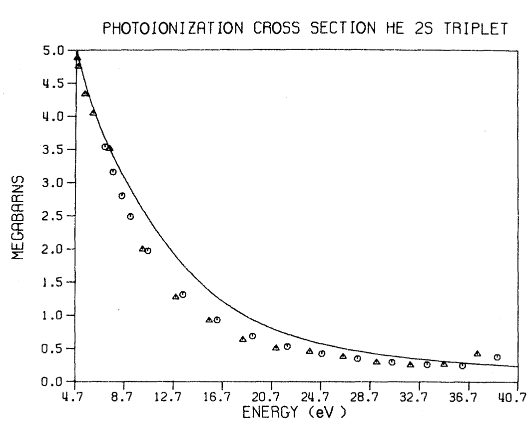

FIG. 2. Photoionization cross sections of the $2\,^3S$ state of helium in Mb. The curve shows the present cross sections obtained by numerical analytic continuation. The triangles and octagons are the calculated results of Norcross (Ref. 8) and Jacobs (Ref. 9), respectively.

TABLE III. Relative probabilities for two-photon emission of the $2\,^1S$ level of helium.

y[a]	$A(y)$[b]	$A(y)$[c]	$A(y)$[d]
0.00	0.0	0.0	0.0
0.05	28.1	24.7	25.2
0.10	65.5	58.2	59.9
0.15	94	83.8	86.4
0.20	115	103	106
0.25	130	116	120
0.30	141	126	130
0.35	149	133	137
0.40	154	138	142
0.45	157	141	145
0.50	158	141	145

[a] $y=\omega_1/\omega_{0f}$, where ω_1 is the frequency of one of the two photons.

[b] Using the definition of the RPA for excited-state–excited-state transition moments of Eq. (12). $A(y)$ is in units of $\sec^{-1}$.

[c] Equations (21) and (22) of text with the initial–final-state experimental energy differences.

[d] Reference 18.

is partly due to the strong ω_{0f} frequency dependence of $A(y)$ rather than the sum over intermediate states in $M(y)$. For example, if we use the experimental ω_{0f} in Eq. (21), the calculated $A(y)$ falls within (2–3)% of the accurate results of Ref. 18. These results are also listed in Table III. The Einstein A coefficient derived from our $A(y)$ of the second column of Table I is 55.6 $\sec^{-1}$ compared with 51.3 $\sec^{-1}$ of Ref. 18. With the $A(y)$ derived from the experimental ω_{0f}, i.e., the third column of Table III, we obtain an A coefficient of 49.7 $\sec^{-1}$.

IV. CONCLUSIONS

We have derived an approximation for transition moments between excited states consistent with the approximations and assumptions normally used to obtain transition moments between the ground and excited states in the random-phase approximation. The basic procedure is to exploit the formal properties of the excitation operators $O^\dagger_{\lambda_i}$ defined on the ground state, i.e., $O^\dagger_{\lambda_i}|0\rangle$, to rewrite the transition moment $\langle\lambda_i|M|\lambda_j\rangle$ as an expectation value of double commutators, Eq. (10), over the ground-state wave function. The resulting expression can then be written in terms of the ground-excited transition amplitudes. Equation (12) can be viewed as an RPA definition of transition moments between excited states.[6] Although for some applications the lower-order TDA or single-excitation CI may suffice, there are cases where a higher-order solution is necessary to calculate excited-state–excited-state transition moments.[7]

The results for the photoionization cross sections of the $2\,^1S$ and $2\,^3S$ metastable states of helium demonstrate some of the useful applications of these discrete oscillator strength distributions for excited-state–excited-state transitions. Most importantly, these results indicate that it is also not necessary to employ continuum basis functions in the calculation of photoionization cross sections of metastable states. This can be very significant for molecular photoionization, where it is very difficult to obtain adequate continuum eigenfunctions. Some immediate applications could be to the photoionization of rare-gas excimers involved in proposed gas lasers, e.g., the He_2 UV laser. From the calculated two-photon emission cross sections of the $2\,^1S$ state helium, the procedure could also be an easy and direct approach to two-photon emission cross sections in molecular systems.

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