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Linear polarizability calculation for rare-gas atoms in the time-dependent local-density approximation with a scissors operator

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We report a modified time-dependent local-density-approximation (TDLDA) calculation of the linear polarizability of rare-gas atoms. The modification we use takes the self-energy into account by introducing a scissors operator; we simply increase the energy differences of the occupied and unoccupied orbitals from the LDA calculation by a constant. The energy shift is (1) estimated with a single oscillator model and (2) determined such that the modified TDLDA with the scissors operator gives the experimental value of the static linear polarizability. The ratio of the energy shift to the lowest LDA energy difference between occupied and unoccupied orbitals for each atom is calculated. These ratios are found to be comparable to the corresponding ratios of the energy shift to the energy gap in the scissors operator in a solid. The modified TDLDA calculation with the scissors operator agrees better with the experimental results, for the frequency dependence of the linear polarizability, than the TDLDA calculation. We apply the Schmidt-Ruedenberg even-tempered Gaussian basis in our calculation and find that the energy-optimized basis set gives a rather poor convergence rate for the linear polarizability. However, a good convergence rate can easily be obtained by adding a few diffuse basis functions to an energy-optimized basis set.

I. INTRODUCTION

The time-dependent local-density approximation (TDLDA) has been used to calculate linear response of rare-gas atoms by several groups$^{1-4}$ since 1980. Within the TDLDA formalism, one can incorporate the dynamic electron-electron interaction into an effective single-particle potential and form a set of self-consistent equations. The inclusion of this local-field correction gives a much better description of the response of a system under the influence of an external field. Zangwill and Soven[2] introduced the TDLDA calculation of the total and partial photoabsorption cross section of rare-gas atoms with success. The TDLDA calculations of the linear polarizability $\alpha(\omega)$ shows that a reasonable agreement with the experiment is obtainable. However, there still exists an obvious discrepancy with the corresponding experimental data. The latest TDLDA calculation by Senatore and Subbaswammy[4] reports an overestimation of the $\alpha(\omega)$ versus ω^2 slope by 50% for the He atom to 14% for the Xe atom compared with the corresponding experimental value. The discrepancy comes from the fact that the TDLDA does not predict optical properties correctly. Several groups$^{5-7}$ have suggested that quasiparticle energies are good predictors of optical properties. Currently, the *GW* approximation is the most sophisticated practical method to obtain the quasiparticle energies in solids. Within the *GW* approximation, the optical excitation frequencies in semiconductors can be predicted to within 0.1 eV of the experimental value. In Si, GaAs, and AlAs, the differences between the computed quasiparticle energy and local-density-approximation (LDA) energy depend weakly on the wave vector **k**. One can simply shift the LDA conduction bands by a constant to reach the quasiparticle results. This is the so-called "scissors operator." The scissors operator has been successfully applied to calculate the dielectric function of Si and Ge (Ref. 8) as well as the dielectric constant and nonlinear susceptibility for a few III–V compounds.[9] The results have shown that the modified TDLDA with the scissors operator consistently yields much better results than the TDLDA.

In this paper we will present our modified TDLDA results for the dynamic linear polarizability with the scissors operator in rare-gas atoms. Our modified TDLDA calculation has a better description of the frequency dependence of the linear polarizability for all rare-gas atoms than the one given by the TDLDA.

The calculation of the linear polarizability for atoms and small molecules has a long history. The most common methods for the polarizability calculation are the uncoupled Hartree-Fock (UCHF) and the coupled Hartree-Fock (CHF) approximations.[10,11] The major difference between the UCHF and CHF methods is that the UCHF approximation completely ignores the correlation effects while the CHF includes mainly first-order correlation effects. To minimize the error in the linear polarizability calculation, the inclusion of the correlation effects is fairly important. Werner and Meyer[12] have conducted a pair-natural-orbital configuration-interaction (PNO-CI) calculation, where the correlation effect is taken into account at the level of the coupled-electron-pair approximation. Their results are within 2% of the corresponding experimental results. Other methods[13] are also developed so that the second- and third-order correlation effects can be taken into account. However, the complication of the methods themselves confined their applications only to small molecules. The LDA is an alternative to the complicated configuration-interaction (CI) family of calculations. It takes the correlation interaction into account in a much simpler form and has already been applied to both small and large systems.

In most published work, only the static polarizabilities of various atoms and molecules are calculated. The static polarizabilities are calculated from either the second derivative of the total energy with respect to the external electric field[14] or the difference of the induced dipole moments at small, finite external field strengths (finite perturbation calculation).[11,12] These methods are limited to static phenomena. For frequency-dependent polarizabilities, one needs to start with a time-dependent perturbation theory. The TDLDA is a time-dependent perturbation theory which is built on the local-density approximation; hence it enables us to study both the static and finite frequency polarizabilities.

To obtain a dependable result for the linear polarizability, it is also important that the wave functions are expanded in an appropriate basis set. We applied an even-tempered Gaussian basis in our calculation. The parameters of the even-tempered Gaussian basis functions have been optimized by Schmidt and Rudenberg[15] from H to Ar atoms for total-energy calculations. As we show below, we must augment these energy-optimized basis functions to obtain good convergence in the linear polarizability calculation.

Previous workers[1-4] solved the TDLDA problem using a numerical solution of the differential equations rather than expanding the wave functions in terms of a basis set. It is simpler to directly solve the differential equation for atoms; but it's hard to apply the same method on molecules. With a long-range goal of studying molecules, we implement the Gaussian basis and gain the advantage of ease of the application of the scissors operator in our modified TDLDA calculation.

The outline of the paper is as follows. We start with a brief overview of the formalism of the modified TDLDA with the scissors operator, where we introduce the single-oscillator model in the estimation of energy shift in the scissors operator. Our results from the TDLDA and modified TDLDA with the scissors operator are then presented. Next we illustrate the convergence rate of the total energy and linear polarizability with energy-optimized Schmidt-Ruedenberg Gaussian basis sets as well as the augmented basis sets. A discussion on the applicability of the scissors operator in rare-gas atoms for the linear polarizability calculation concludes the paper.

II. MODIFIED TDLDA WITH A SCISSORS OPERATOR

A. Formalism

Our TDLDA calculation begins by solving for the ground-state orbital eigenvalues and their corresponding eigenfunctions. The Kohn-Sham[16] eigenvalue equation (in atomic units) is applied,

$$(-\tfrac{1}{2}\nabla^2+V_{\mathrm{ext}}+V_{hc}+\mu_{\mathrm{xc}})\psi_{nlm}(\mathbf{r})=\varepsilon_{nl}\psi_{nlm}(\mathbf{r})\ , \tag{2.1}$$

$$V_{\mathrm{ext}}=-\frac{Z}{r}\ , \tag{2.2}$$

$$V_{hc}=\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\ , \tag{2.3}$$

where the Ceperley-Alder exchange-correlation energies are used in our calculation to approximate the exchange-correlation potential μ_{xc}.[17] In the equation, ε_{nl} and $\psi_{nlm}(\mathbf{r})$ are taken to be the eigenenergy and eigenfunction for the orbital with quantum numbers nlm, $n(\mathbf{r})$ is the number density of the electrons. The wave functions $\psi_{nlm}(\mathbf{r})$ are expanded in a Gaussian basis set; specifically,

$$\psi_{nlm}(\mathbf{r})\sum_{i=1}^{N_l}c_{inl}\varphi_{ilm}(\mathbf{r})=R_{nl}(r)Y_{lm}(\theta,\phi) \tag{2.4}$$

and

$$\varphi_{ilm}(\mathbf{r})=b_{il}r^l\exp(-\zeta_{il}r^2)Y_{lm}(\theta,\phi)\ . \tag{2.5}$$

In Eq. (2.4), N_l is the total number of the Gaussian functions used to expand the wave functions with angular-momentum quantum number l. The coefficients c_{inl} and b_{il} are introduced to normalize the wave functions ψ_{nlm} and the basis functions φ_{ilm}, respectively. Orbitals with the same angular-momentum quantum number l are expanded in the same set of the Gaussian basis functions. Details on choosing the Gaussian basis parameters ζ_{il} will be discussed in the next section. The calculated LDA ground-state eigenvalues ε_{nl} and their corresponding wave functions $\psi_{nlm}(\mathbf{r})$ are then used in the calculation of the linear response of the system.

The next step of the linear polarizability calculation requires the perturbed wave function $\psi^{(1)}_{nlm,\pm\omega}$ obtained from the following equation:

$$(\varepsilon_{nl}\pm\omega-H_0)\psi^{(1)}_{nlm,\pm\omega}=V_{\pm\omega}(\mathbf{r})\psi_{nlm}\ , \tag{2.6}$$

a result of first-order perturbation theory. Here $V_{\pm\omega}(\mathbf{r})$ includes the external perturbation potential, the induced Hartree or Coulomb potential, and the induced exchange-correlation potential. If the external electric field is written as

$$\mathbf{E}=E_0\hat{\mathbf{z}}\cos(\omega t)=\tfrac{1}{2}E_0\hat{\mathbf{z}}(e^{i\omega t}+e^{-i\omega t})\ , \tag{2.7}$$

then

$$V_\omega(\mathbf{r})=\tfrac{1}{2}E_0r\cos\theta+\int\frac{\delta n(\mathbf{r}',\omega)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+\frac{\partial V_{\mathrm{xc}}}{\partial n}\delta n(\mathbf{r},\omega)\ . \tag{2.8}$$

The latter two depend on the induced density $\delta n(\mathbf{r},\omega)$, given by

$$\delta n(\mathbf{r},\omega)=2\sum_{n,l,m}^{\mathrm{occ}}[\psi^{(1)}_{nlm,\omega}(\mathbf{r})\psi_{nlm}(\mathbf{r})^*+\psi^{(1)*}_{nlm,-\omega}(\mathbf{r})\psi_{nlm}(\mathbf{r})]\ . \tag{2.9}$$

Equations (2.6), (2.8), and (2.9) are solved self-consistently for the induced density $\delta n(\mathbf{r},\omega)$. The numerical method used to solve for $\delta n(\mathbf{r},\omega)$ is to expand the induced wave function $\psi^{(1)}_{nlm,\pm\omega}(\mathbf{r})$ in terms of the same set of the Gaussian basis Eq. (2.5):

$$\psi^{(1)}_{nlm,\pm\omega}(\mathbf{r})=\sum_{i=1}^{N_{l+1}}\left[\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}\right]^{1/2}\times d_{i,n,l+1,\pm\omega}\varphi_{i,l+1,m}(\mathbf{r})+\sum_{i=1}^{N_{l-1}}\left[\frac{(l+m)(l-m)}{(2l+1)(2l-1)}\right]^{1/2}\times d_{i,n,l-1,\pm\omega}\varphi_{i,l-1,m}(\mathbf{r})\ . \tag{2.10}$$

The factors in the square roots arise from the following relation[18] [note, $V_\omega(\mathbf{r})=V_\omega(r)\cos\theta$]:

$$(\cos\theta)Y_{lm}=\left[\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}\right]^{1/2}Y_{l+1,m}+\left[\frac{(l+m)(l-m)}{(2l+1)(2l-1)}\right]^{1/2}Y_{l-1,m}\ . \tag{2.11}$$

The coefficients d are independent of the quantum number m. The linear polarizability can be obtained from its definition with the following formula:

$$\alpha(\omega)=-\frac{2}{E_0}\int z\delta n(\mathbf{r},\omega)d\mathbf{r}=-\frac{2}{E_0}\sum_{n,l,m}\sum_{n',l'}(f_{nlm}-f_{n'l'm})\frac{\langle\psi_{nlm}|r\cos\theta|\psi_{n'l'm}\rangle\langle\psi_{n'l'm}|V_\omega|\psi_{nlm}\rangle}{\varepsilon_{nl}-\varepsilon_{n'l'}+\omega}\ . \tag{2.12}$$

The fact that $V_\omega=V_{-\omega}$ is used to derive the above expression, where f_{nlm} is the occupation number for the orbital nlm. The value of f_{nlm} is 2 (spin freedom) for an occupied state and 0 for an unoccupied state. Also, ψ_{nlm} and ε_{nl} are the LDA eigenstate wave function and eigenenergy as in Eq. (2.1).

Optical processes necessarily involve quasiparticles.[5-7] The LDA formalism, designed to calculate the ground-state energy, does not compute the quasiparticle energies. Instead, the nonlocal and energy-dependent self-energy should replace the local exchange-correlation potential in the Kohn-Sham equation. Currently, the *GW* approximation is used to compute the self-energies in solids. It has been found that the quasiparticle wave function of the *GW* calculations are in very good agreement with the wave function of the LDA calculations.[6] In some solids, e.g., Si, GaAs, and AlAs, the difference between the quasiparticle energy and the LDA eigenenergy depends weakly on the wave vector.[7] One can simply apply a scissors operator to shift the LDA conduction band up by a constant to obtain the corresponding quasiparticle energy band.

We introduce the scissors operator in our study for the linear response of the rare-gas atomic system to increase the energy difference between the occupied and the unoccupied energy levels by a constant Δ, i.e., Eq. (2.12) is replaced by the following equation:

$$\alpha(\omega)=-\frac{2}{E_0}\sum_{n,l,m}\sum_{n',l'}(f_{nlm}-f_{n'l'm}\frac{\langle\psi_{nlm}|r\cos\theta|\psi_{n'l'm}\rangle\langle\psi_{n'l'm}|V_\omega|\psi_{nlm}\rangle}{\varepsilon_{nl}-\varepsilon_{n'l'}\pm\Delta+\omega}\ . \tag{2.13}$$

Here, the energy shift Δ is defined to be positive and the ± sign in the above equation is to ensure that the scissors operator always increases[5] the energy difference between occupied and unoccupied energy levels. Notice that the contribution to the linear polarizability α from the transitions between two occupied states or two unoccupied states is zero. A simple single oscillator model is applied to estimate the energy shift Δ.

B. Single-oscillator method

The single-oscillator method is a simple but surprisingly successful way to describe the low-frequency electronic dielectric function in many systems. Wemple and DiDomenico[19] fit the dielectric function $\varepsilon(\omega)$ of more than 100 different solids with a single-oscillator model using the relation

$$\varepsilon(\omega)=E_dE_0/(E_0^2-\hbar^2\omega^2)\ . \tag{2.14}$$

In the formula, E_0 is the single-oscillator energy and E_d is a parameter which depends on the crystal structure and ionicity of the solid.

We applied this idea in atoms to estimate the energy shift needed in the scissors operator. In the single-oscillator model, the imaginary part of the polarizability $\alpha(\omega)$, which is directly related to the absorption cross section, is simply a δ function

$$\mathrm{Im}\alpha(\omega)=\frac{\pi K}{2}\delta(\omega-\omega_0)\ , \tag{2.15}$$

where K and ω_0 are the parameters to be determined. The physical meaning of ω_0 is the resonance energy of the single oscillator. The Kramers-Kronig relation leads to

$$\mathrm{Re}\alpha(\omega)=\frac{K\omega_0}{\omega_0^2-\omega^2}\ . \tag{2.16}$$

It is easy to see that Eqs. (2.14) and (2.16) have the same form. For small frequencies, the real part of α is

$$\mathrm{Re}\alpha(\omega)\approx\frac{K}{\omega_0}+\frac{K}{\omega_0^3}\omega^2\ . \tag{2.17}$$

The parameters K and ω_0 are determined so that Eq. (2.17) fits the TDLDA results,

TABLE I. TDLDA calculation of the linear polarizability for the rare-gas atoms. In the region well below the absorption threshold, $\alpha(\omega)$ vs ω^2 is a straight line with a slope $\partial\alpha(\omega)/\partial(\omega^2)$. Our TDLDA results are compared with those of Senatore and Subbaswammy (Ref. 4).

	$\alpha(0)$ (Å^3)			$\frac{\partial\alpha(\omega)}{\partial(\omega^2)}$ $[10^{-3}$ Å^3/(eV)$^2]$		
	Present	Ref. 4	Expt.	Present	Ref. 4	Expt.
He	0.246	0.246	0.205	0.49	0.50	0.32
Ne	0.452	0.452	0.395	0.89	0.91	0.59
Ar	1.78	1.78	1.64	7.3	7.5	5.8
Kr	2.65	2.67	2.48	14.4	14.8	12.1
Xe	4.25	4.26	4.04	31.1	31.6	27.6

$$\alpha(0)^{\mathrm{TDLDA}} = \frac{K}{\omega_0}$$

and

$$\frac{\partial\alpha(\omega)^{\mathrm{TDLDA}}}{\partial(\omega^2)} = \frac{K}{\omega_0^3} . \tag{2.18}$$

To approximate the quasiparticle energy levels, ω_0 is shifted by a constant Δ^{model} in the single oscillator model. We replace ω_0 in Eq. (2.18) by $\omega_0+\Delta$ such that the model reproduces the experimental static polarizability,

$$\frac{K}{(\omega_0+\Delta^{\mathrm{model}})} = \alpha(0)^{\mathrm{expt}} . \tag{2.19}$$

The actual energy shift $\Delta^{\mathrm{scissors}}$ for our modified TDLDA calculation in Eq. (2.14) is determined so that when the energies of the unoccupied orbitals from the LDA calculation are shifted up by $\Delta^{\mathrm{scissors}}$ with respect to the occupied orbital energies, the modified TDLDA calculation will reproduce the experimental result of the static linear polarizability. It turns out that the single oscillator model Δ^{model} provides a good guide for the energy shift $\Delta^{\mathrm{scissors}}$.

C. Results and analysis

Our TDLDA results (without scissors) for the linear polarizability of the rare-gas atoms are shown in Table I. Our calculated static linear polarizabilities agree with Senatore and Subbaswammy's[4] corresponding results within 1%. (We both use the Ceperley-Alder exchange-correlation results but different numerical calculation methods.) This is as good as if not better agreement than achieved[3] among the calculations of Stott and Zamemba,[1] Zangwill and Soven[2] and Mahan[3] all of whom used the Gunnarsson-Lundquist[20] parametrization of the exchange-correlation potential.

We compare the experimental data[21] with our results from the modified TDLDA with the scissors operator and also with the results from the single-oscillator model. As described in Sec. II B, the parameters K and ω_0 in the single oscillator model are determined so that the model reproduces our TDLDA result of the static linear polarizability. The energy shift in the single-oscillator model Δ^{model} is estimated such that the model will give the exact experimental result of the static linear polarizability. With this energy shift, the model can predict the frequency dependence of the linear polarizability. As shown in Table II, the agreement with the model's predicted slope and the experimental slope is surprisingly good; except for He, discrepancies are no more than 3%.

In our modified TDLDA calculation with a scissors operator, the energy shift between the occupied and unoccupied energy levels is determined so that the modified TDLDA will give the exact experimental value of the static linear polarizability. Keeping the same energy shift, we calculated the frequency dependence of the linear polarizability $\alpha(\omega)$. In the region well below the absorption line, $\alpha(\omega)$ depends linearly on ω^2. The calculated slope $\partial\alpha(\omega)/\partial(\omega^2)$ is compared with the experimen-

TABLE II. Modified TDLDA calculation of the linear polarizability for the rare-gas atoms. The frequency dependence of the linear polarizability both from the modified TDLDA, which shifts the energy differences between the occupied and unoccupied states with the scissors operator and from the single-oscillator model described in the text, are given. In either case (scissors or model), the relevant parameters are adjusted to give the experimental value of the $\alpha(0)$. The parameter K is defined in Eq. (2.15).

	$\frac{\partial\alpha(\omega)}{\partial(\omega^2)}$ $[10^{-3}$ Å^3/(eV)$^2]$			Δ (eV)		K [Å^3 (eV)^2]
	Scissors	Model	Expt.	Scissors	Model	Model
He	0.26	0.28	0.32	4.8	4.5	5.5
Ne	0.51	0.59	0.59	3.8	3.3	10.2
Ar	5.2	5.8	5.8	1.6	1.3	27.8
Kr	11.0	11.8	12.1	1.15	0.9	35.9
Xe	25.0	26.9	27.6	0.75	0.6	49.7

TABLE III. Energy shift in the scissors operator. In the table, Δ^{model} and $\omega_0^{\mathrm{model}}$ are the estimated energy shift and energy gap in the single-oscillator model given in Table II; $\Delta^{\mathrm{scissors}}$ is the energy shift in our modified TDLDA calculation; ω_0^{LDA} is the lowest energy difference of the occupied and unoccupied orbitals in our LDA ground-state calculation. The last two columns are the ratio of the energy shift to the energy gap in the single-oscillator model and in the modified TDLDA with the scissors operator. The ranges of the ratio are comparable in solids and atoms.

	ω_0 (eV)		Δ/ω_0	
	LDA	Model	Scissors	Model
He	16.0	22.4	0.30	0.20
Ne	13.5	22.5	0.28	0.15
Ar	10.1	15.6	0.16	0.08
Kr	9.0	13.6	0.13	0.07
Xe	8.0	11.6	0.09	0.05

tal slope. It turns out that the slope calculated using the modified TDLDA agrees better with the experimental slope than the one from the TDLDA calculation. The discrepancies of the TDLDA slope with respect to the experimental slope are 51%, 51%, 26%, 19%, and 13% and the corresponding discrepancies for the modified TDLDA are −19%, −14%, −10%, −9%, and −9% for the He to Xe series.

Tables III and IV are a comparison of the scissors operator in the rare-gas atoms with the one in a solid. The ratio of the energy shift and the lowest energy difference between the occupied and unoccupied states is calculated for each rare-gas atom in Table III. It ranges from 0.09 to 0.30. Table IV gives the ratio of the energy shift in the scissors operator to the energy gap in the diamond crystal, which ranges from 0.22 to 0.59 for different **k** points. The range of the ratio $\Delta/\varepsilon^{\mathrm{gap}}$ is comparable in both solid and the rare-gas atoms. The TDLDA results agree better with the experimental data for the heavier atoms and need a smaller energy shift in the scissors operator, even in comparison to the energy scale of the valence electrons.

Figure 1 shows the linear relationship of the $\alpha(\omega)$ versus ω^2 in a semilogarithmic scale. One can see that the linear relationship holds well in the region well below the absorption threshold. The data show a small upward trend as the frequency approaches the absorption limit. The TDLDA calculation overestimates the experimental slope while the modified TDLDA with scissors operator overcorrects the TDLDA slope. If we assume[22] that the wave functions from the LDA and the *GW* calculation are almost identical in atoms, then the overcorrection of the TDLDA slope can be explained by the way we determine the energy shift in the scissors operator. In the available *GW* calculation in the solid case, the energy shift Δ generally increases as the energy gaps from the LDA calculation increases.[6] In our case, this means that Δ should increase as $|\varepsilon_{nl}-\varepsilon_{n'l'}|$ in Eq. (2.13) increases. We choose the energy shift Δ to be a constant so that the modified TDLDA with the scissors operator will give the exact static linear polarizability. The Δ value we used in our modified TDLDA calculation is therefore an average value of the Δ as a function of $\varepsilon_{nl}-\varepsilon_{n'l'}$ so that it is higher than the energy shift needed for the small $\varepsilon_{nl}-\varepsilon_{n'l'}$ values. If we ignore the induced potentials in the linear polarizability calculation (independent-particle model), it is easy to find an analytical expression for the $\alpha(\omega)$ versus ω^2 slope, $\frac{1}{2}\partial^2\alpha(\omega)/\partial\omega^2$. From Eq. (2.13), the slope depends on $(\varepsilon_{nl}-\varepsilon_{n'l'}\pm\Delta+\omega)^{-3}$ rather than the $(\varepsilon_{nl}-\varepsilon_{n'l'}\pm\Delta+\omega)^{-1}$ for the linear polarizability. The slope depends more on small $|\varepsilon_{nl}-\varepsilon_{n'l'}|$ values than the linear polarizability. Since the constant energy shift Δ used in the modified TDLDA calculation is higher than the correction needed for small values of $|\varepsilon_{nl}-\varepsilon_{n'l'}|$, the slope of the modified TDLDA tends to be lower than it should.

TABLE IV. Scissors operator in diamond. Data are from Ref. 7; $\Delta=\varepsilon^{GW}-\varepsilon^{\mathrm{LDA}}$ are the self-energy corrections; the $\varepsilon^{\mathrm{LDA}}$ are the LDA eigenvalue differences from the valence-band maximum.

Diamond	Δ (eV)	$\varepsilon^{\mathrm{LDA}}$ (eV)	Δ/ε
$\Gamma_{15,c}$	2.01	5.50	0.37
$X_{4,v}\rightarrow X_{1,c}$	2.29	10.44	0.22
$L_{1,c}$	2.10	8.00	0.26
E_g	2.06	3.48	0.59

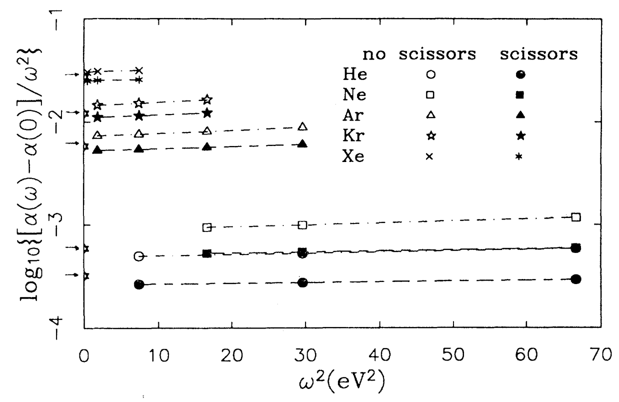

FIG. 1. The frequency dependence of the linear polarizability for the rare-gas atoms. If $\alpha(\omega)$ and ω^2 had a strict linear relationship, the curves would be straight lines parallel to the horizontal axis. The arrows around the vertical axis point to the corresponding experimental values, which lie in between the TDLDA (without scissors) and the modified TDLDA (with scissors) curves.

III. CONVERGENCE STUDY OF THE LINEAR POLARIZABILITY WITH GAUSSIAN BASIS

Independent of the concerns of an appropriate treatment of the correlation interaction, the selection of appropriate basis functions has always been a major difficulty in linear polarizability calculations. Compared to the considerable study on constructing minimal basis sets for the total-energy calculation of atomic and molecular systems, there is little published work on the corresponding linear polarizability calculation. Most basis functions used in the linear polarizability calculation are augmented from the energy-optimized basis sets by adding a few diffuse basis functions with small exponents. The simplest way to choose the diffuse basis functions is to continue an approximate geometric series in the augmented basis. To obtain some insights into a good choice of basis functions for the linear polarizability calculation, Zeiss *et al.*[13] analytically solved the perturbed wave function of the H atom under the influence of an external static field. Further, a scale factor, introduced as a parameter in the perturbed H atom wave functions is used to approximate the perturbed wave functions for all atoms. The scale factor can be determined so that the approximated perturbed wave functions reflect the range of the outermost orbital of a particular atom. The approximated perturbed wave functions are fitted by a set of Gaussian basis functions with the least-squares method. These Gaussian basis functions (field-induced polarization functions) are then used with an energy-optimized basis set in the linear polarizability calculation. There also exist basis sets obtained by minimizing the Hartree-Fock (HF) energy of the molecule in the presence of a weak electric field.[23] All of these methods produce a similar choice of the exponents for the diffuse basis functions needed in the linear polarizability calculation.

There are many choices of the energy-optimized Gaussian basis.[24] All these optimized Gaussian basis sets are constructed to describe the occupied wave functions. We concentrate on the even-tempered Gaussian basis in which [cf. Eq. (2.5)] the ζ are

$$\zeta_{il}=\alpha_l\beta_l^{i-1}, \quad i=1,2,\ldots,N_l \; . \tag{3.1}$$

For orbitals with quantum number l, there are three parameters α_l, β_l, and the total number of the basis functions N_l. For the total-energy calculation, Schmidt and Reudenberg[15] parametrized α_l and β_l as a function of the number of the basis functions N_l for all elements from H to Ar. With this scheme, one can condense the three parameters α_l, β_l, and N_l into one for each l.

It is more convenient to think in terms of the real space rather than the ζ space covered by a Gaussian basis set. Since ζ is proportional to $1/r^2$, the Gaussian basis function with small ζ values covers the large-r region. For the linear polarizability calculation, both the occupied and low-lying unoccupied orbital wave functions need to be fitted well. This means that the basis functions for the linear polarizability calculation need to cover a larger-r region than the energy-optimized basis functions provided. It is logical to think that for the polarizability calculation, some diffuse basis functions with small ζ need to be added to the energy-optimized basis set.

Before augmenting the energy-optimized basis set, we present the convergence rate of the linear polarizability using an energy-optimized basis set. Figure 2 shows the convergence rate of the total energy and static linear polarizability of the Ne atom with the Schmidt-Rudenberg energy-optimized even-tempered basis set. In the Schmidt-Ruedenberg scheme, only the parameters for the occupied orbitals are given for each atom. We choose to use the basis functions with small-ζ values of the outermost occupied orbital with angular-momentum quantum number l to describe the unoccupied orbital $l+1$. One can easily see that the convergence rate of the total energy is rather good while the convergence rate of the linear polarizability is poor. With a large basis set of total 110 functions ($40s37p33d$), the linear polarizability is 0.449 Å^3, while the "exact" theoretical value is 0.452 Å^3. It is obvious to see that an augmentation to the energy-optimized basis set is needed.

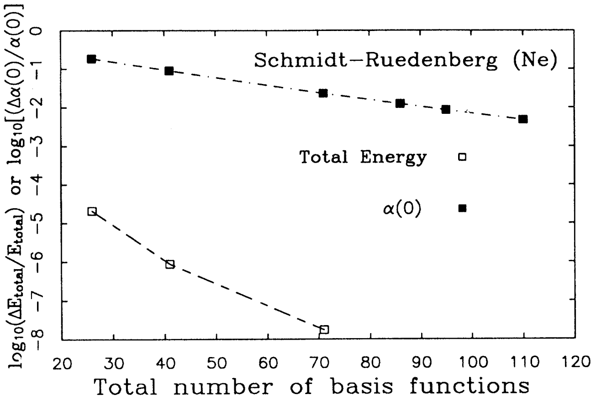

FIG. 2. Convergence study of a Ne atom with energy-optimized Schmidt-Ruedenberg basis sets. The vertical axis indicates either the logarithm of the relative discrepancy of the total energy or the static linear polarizability $\alpha(0)$. The horizontal axis is the total number of the basis functions, which is the sum of the number of basis functions for the s, p, and d orbitals (not counting the degenerate subshells separately). The combinations of the basis functions are $12s9p5d$, $17s14p10d$, $27s24p20d$, $32s29p25d$, $35s32p28d$, and $40s37p33d$.

We choose to add a few diffuse basis functions such that the augmented basis set is still an even-tempered one. For each atom, the N_l are chosen so that they give a reasonably good value for the total energy. The parameters in the even-tempered basis set α_l and β_l are then calculated according to the Schmidt-Ruedenberg formula[15] for the fixed N_l. These β_l values are used to add a few diffuse basis functions to the energy-optimized basis set N_l to form a new even-tempered basis. The difference between the augmented even-tempered basis and the energy-optimized even-tempered basis is that the β_l values are unchanged when more basis functions are added in the augmented basis set. Figure 3 illustrates the convergence of the total energy and the linear polarizability with the augmented basis set for He, Ne, and Ar. The convergence rate of the linear polarizability improves dramatically compared to the one with the energy-optimized basis set. For a neon atom, for example, with a total of only 30 basis functions ($14s10p6d$), the linear polarizability has already reached the exact theoretical value of 0.452 Å^3. It is not surprising that the additional basis functions only slightly improve the total energy. The added basis functions in the augmented even-tempered set describe the large-r region, which is beyond

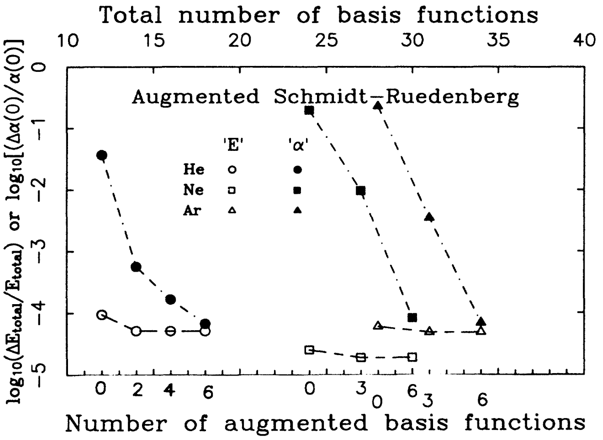

FIG. 3. Convergence study of He, Ne, and Ar atoms with the augmented Schmidt-Ruedenberg basis functions. The vertical axis indicates either the logarithm of the relative discrepancy of the total energy or the static linear polarizability $\alpha(0)$. The symbols E and α stand for $\log_{10}(\Delta E_{\text{tot}}/E_{\text{tot}})$ and $\log_{10}[\Delta\alpha(0)/\alpha(0)]$, respectively. The top axis is the total number of the basis functions, which is the sum of the number of basis functions for the s, p, and d orbitals. The bottom axis indicates the total number of the extra diffuse basis functions added. The combination of the basis functions are for He: $8s4p$, $9s5p$, $10s6p$, and $11s7p$; for Ne: $12s8p4d$, $13s9p5d$, and $14s10p6d$; and for Ar: $16s8p4d$, $17s9p5d$, and $18s10p6d$.

the range of the occupied wave functions. For the Kr and Xe atoms, there is no energy-optimized even-tempered basis set we are aware of; rather, we used large even-tempered basis sets with small β_l values to ensure the well-converged values for the linear polarizability.

Roughly speaking, one needs to add 2–3 more diffuse basis functions to the energy-optimized basis set to obtain 1% accuracy for the linear polarizability. Approximately, 14 ($9s5p$), 27 ($13s9p5d$), and 31 ($17s9p5d$) basis functions are needed for He, Ne, and Ar, respectively. It is possible to find a small yet arbitrary basis set which gives a good value for the linear polarizability but a poor value for the total energy. Such a basis set usually gives a poor description of the exact wave functions. To construct a minimal basis set for the linear polarizability calculation, the approximate wave functions formed by the basis set need to have maximal overlap with the exact wave functions.[12]

IV. SUMMARY

The modified TDLDA calculation of the linear polarizability of the rare-gas atoms involves introducing the scissors operator to approximate the self-energy operator of a *GW* calculation. The energy shift in the scissors operator is first estimated by the single oscillator model and then determined such that the modified TDLDA with this energy shift reproduces the experimental value of the static linear polarizability. The frequency dependence of the linear polarizability, $\partial\alpha(\omega)/\partial(\omega^2)$, of the modified TDLDA has a better overall agreement with the experiment than of the TDLDA. Curiously, the results given by the single-oscillator model are in better agreement with the experiment than the modified TDLDA.

For simplicity, we applied the scissors operator at only the most primitive level, i.e., we shift all the energy differences of the occupied and unoccupied orbitals by a constant Δ which ignores any energy dependence of the energy shift. We found that our modified TDLDA calculation overcorrects the TDLDA results. The applicability of using the scissors operator to take the self-energy into account for the atom is based on the results of the *GW* calculations for solids and also from the fact that the scissors operator works well in some solids.[8] So far there has not been an atomic *GW* calculation to our knowledge. We believe the remaining errors in the excitation energies contribute most of the discrepancies in our modified TDLDA calculation. From the fact that the TDLDA predicts the photoabsorption cross section[2] and asymmetry parameters[25] well, we conclude that the wave functions themselves from the LDA calculation probably are adequate.

The convergence study shows that the energy-optimized basis set needs to be augmented with a few diffuse basis functions to produce a converged calculation of the linear polarizability.

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