

New formalism for determining excitation spectra of many-body systems

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We present a new general formalism for determining the excitation spectrum of interacting many-body systems. The basic assumption is that the number of the excitations is equal to the number of sites. Within this approximation, it is shown that the density-density response functions with two different pure-imaginary energies determine the excitation spectrum. The method is applied to the valence electrons of sodium clusters of differing sizes in the time-dependent local-density approximation (TDLDA). A jellium-sphere background model is used for the ion cores. The excitation spectra obtained in this way represent well the excitation spectra given by the full TDLDA calculation along the real energy axis. Important collective modes are reproduced very well.

I. INTRODUCTION

In interacting many-fermion systems, the single-particle excitations following the addition or removal of one particle are called quasiparticles. In solids, quasiparticles of interacting valence electrons form energy bands, which can be observed directly using photoelectron spectroscopy. In finite systems, the quasiparticle concept is also useful. The Hohenberg-Kohn density-functional theory¹ with the Kohn-Sham local-density approximation² (LDA) has been widely used not only for calculating energy bands of solids but also for electronic-structure calculations of atoms and molecules. Recently, the Hybertsen-Louie approach³ based on the Hedin *GW* approximation⁴ has been used successfully to calculate the quasiparticle energies of solids^{3,5-7} and clusters.⁸

In addition to the single-particle excitations, the interacting particles exhibit collective modes, which conserve the number of the particles and often have clear classical analogs. One of the most studied collective modes is a plasmon in solids, which can be detected by the electron-energy-loss spectroscopy. A plasmon corresponds to a classical longitudinal wave and is often treated quantum mechanically by the random-phase approximation (RPA) in linear-response theory.⁹ Collective modes are also known to exist in finite systems. The giant dipole resonance of the nuclei is believed to be the collective motion of the protons relative to the neutrons.¹⁰ The giant resonances of *4d* electrons in atoms have also been measured.¹¹ A recent photoabsorption-cross-section experiment¹² has revealed the presence of the collective modes of valence electrons in sodium clusters. These are associated with surface plasma resonances.

In the present work, we will consider the excitation spectra of nonmagnetic many-electron systems. In the linear-response regime (adopting units in which $\hbar=1$),

the generalized susceptibility of the electron system is equivalent to the retarded density-density response function:¹³

$$\chi(\mathbf{r}, \mathbf{r}'; t - t') = -i\Theta(t - t') \langle 0 | [\hat{n}(\mathbf{r}, t), \hat{n}(\mathbf{r}', t')] | 0 \rangle, \quad (1)$$

where Θ is the step function, \hat{n} is the electron density operator, and $|0\rangle$ is the exact ground state of the system. The poles of $\chi(\mathbf{r}, \mathbf{r}'; E)$, the density-density response function in energy space, give the energies of excitations which conserve the number of the particles, that is, collective modes and other single-particle-hole pair excitations. In the interacting many-electron systems, $\chi(\mathbf{r}, \mathbf{r}'; E)$ has to be calculated in some approximate way, for instance, RPA, the time-dependent local-density approximation (TDLDA),^{14,15} the Hedin *GW* approximation, and so on.

In the present paper, we discuss a new general and pragmatic formalism to approximate the $\chi(\mathbf{r}, \mathbf{r}'; E)$ on the whole real-energy axis from the temperature density-density response function (as the temperature $T \rightarrow 0$) with only two different pure imaginary energies; $\chi(\mathbf{r}, \mathbf{r}'; iy_1)$ and $\chi(\mathbf{r}, \mathbf{r}'; iy_2)$ ($0 < y_1 < y_2$).¹⁶ (The temperature density-density response function is the analytic continuation of the retarded function and therefore the same expression χ will be used throughout the paper.) The present procedure can be applied to $\chi(\mathbf{r}, \mathbf{r}'; iy)$ calculated in any approximation. In this work, the new method is applied to the TDLDA χ of valence electrons in sodium clusters. The jellium-sphere background model for positive ion cores, which is known to work for simple-metal clusters,¹⁷ is used. The dynamical dipole polarizabilities calculated from the χ in the present formalism are compared with the full TDLDA calculation along the real energy axis, with emphasis on the positions and the oscillator strengths of the collective resonances.

In Sec. II the new formalism is described in detail. After a brief summary of the TDLDA formalism, the results of the new formalism applied to sodium clusters, Na_2 , Na_8 , Na_{18} , Na_{20} , Na_{34} , and Na_{40} , are given in Sec. III. In Sec. IV, we discuss the advantages of the present formalism. Section V contains the conclusion of this paper.

II. NEW FORMALISM FOR EXCITATION SPECTRUM

After the Fourier transformation with respect to time, the retarded density-density response function in energy space is given by

$$\chi(\mathbf{r}, \mathbf{r}'; E) = \sum_m \left[\frac{\langle 0 | \hat{n}(\mathbf{r}) | m \rangle \langle m | \hat{n}(\mathbf{r}') | 0 \rangle}{E - \omega_m + i\delta} - \frac{\langle 0 | \hat{n}(\mathbf{r}') | m \rangle \langle m | \hat{n}(\mathbf{r}) | 0 \rangle}{E + \omega_m + i\delta} \right], \quad (2)$$

where ω_m is the excitation energy from the ground state $|0\rangle$ to the m th excited state of the system, $|m\rangle$, and δ is a positive infinitesimal. Therefore, the poles of χ give the excitation energies of the system. In a nonmagnetic system, we can always use real eigenfunctions both for the ground state and for the excited states. Hence, we can rewrite Eq. (2) as

$$\chi(\mathbf{r}, \mathbf{r}'; E) = \sum_m \langle 0 | \hat{n}(\mathbf{r}) | m \rangle \left[\frac{1}{E - \omega_m + i\delta} - \frac{1}{E + \omega_m + i\delta} \right] \times \langle m | \hat{n}(\mathbf{r}') | 0 \rangle. \quad (3)$$

For noninteracting systems, the excitation energies are equal to the differences between the particle and hole energies. The matrix elements of the density operator between the ground state and the excited states are the products of the wave functions of the particle and the hole being considered. For the interacting systems, however, the expression (3) is only a formal device since it is not straightforward to calculate the excitation energies nor the matrix elements even if $\chi(\mathbf{r}, \mathbf{r}'; E)$ is known for a given E in some approximation. The formalism presented here provides a new approximate way to make the above expression for χ useful.

For convenience, we will use matrix notation

$$[\underline{X}(z)]_{\mathbf{r}, \mathbf{r}'} = \chi(\mathbf{r}, \mathbf{r}'; z), \quad (4)$$

$$\underline{N}_{m, \mathbf{r}} = \langle m | \hat{n}(\mathbf{r}) | 0 \rangle = \langle 0 | \hat{n}(\mathbf{r}) | m \rangle. \quad (5)$$

$\underline{X}(z)$ with $z = E + i\delta$ ($\delta \rightarrow 0$) and $z = iy$ represents the retarded density-density response function and the temperature density-density response function, respectively. Then, Eq. (3) gives

$$-\frac{1}{2}\underline{X}(iy) = \underline{N}^T \underline{Y}(iy) \underline{N}, \quad (6)$$

where \underline{N}^T is the transpose of \underline{N} , and \underline{Y} is a diagonal matrix:

$$[\underline{Y}(iy)]_{mn} = \delta_{mn} \frac{\omega_m}{y^2 + \omega_m^2}. \quad (7)$$

Here, δ_{mn} is Kronecker's delta. Since every excitation energy is positive, the square-root matrix of \underline{Y} can be naturally defined as

$$[\underline{Y}^{1/2}(iy)]_{mn} = \delta_{mn} ([\underline{Y}(iy)]_{mm})^{1/2}. \quad (8)$$

Using the new matrix

$$\underline{M}(iy) \equiv \underline{Y}^{1/2}(iy) \underline{N}, \quad (9)$$

Eq. (6) can be written as

$$-\frac{1}{2}\underline{X}(iy) = \underline{M}^T(iy) \underline{M}(iy). \quad (10)$$

The first step of our formalism is to calculate the density-density response function at some pure imaginary energy iy_1 and to diagonalize the real symmetric matrix $-\frac{1}{2}\underline{X}(iy_1)$:

$$-\frac{1}{2}\underline{X}(iy_1) = \underline{P} \underline{E} \underline{P}^T, \quad (11)$$

where $\underline{E}(iy_1)$ is a diagonal matrix with an eigenvalue $e_{\mathbf{r}}$ on each diagonal element and $\underline{P}(iy_1)$ is an orthogonal matrix with an eigenvector on each column. Combining Eqs. (10) and (11), we can obtain

$$\underline{E} = (\underline{M} \underline{P})^T (\underline{M} \underline{P}), \quad (12)$$

or

$$e_{\mathbf{r}} = \sum_m a_{m, \mathbf{r}}^2, \quad (13)$$

where

$$a_{m, \mathbf{r}} = [\underline{M} \underline{P}]_{m, \mathbf{r}}. \quad (14)$$

Therefore, every $e_{\mathbf{r}}$ is positive and again we can define the diagonal square-root matrix $\underline{E}^{1/2}$. Then, it is easy to show

$$\underline{M}(iy_1) = \underline{Q}^T \underline{E}^{1/2} \underline{P}^T. \quad (15)$$

Here, $\underline{Q}(iy_1)$ is some row-orthogonal matrix satisfying

$$\underline{Q} \underline{Q}^T = \underline{1}, \quad (16)$$

where $\underline{1}$ is the unit matrix.

To obtain \underline{Q} , we assume that the number of excitations (m) is equal to the number of sites (\mathbf{r}). (In the interacting many-body systems, the number of the excitation is generally much larger than the number of sites.) Then, all the matrices are square and \underline{Q} is an ordinary orthogonal matrix ($\underline{Q} \underline{Q}^T = \underline{Q}^T \underline{Q} = \underline{1}$). Within this approximation, χ with another pure imaginary energy, iy_2 ($y_2 > y_1$), determines the matrix \underline{Q} , which now depends not only on y_1 but also on y_2 . To see this, let us define the new matrix $\underline{A}(iy_1, iy_2)$ as

$$\underline{A} \equiv \underline{E}^{-1/2} \underline{P}^T [-\frac{1}{2}\underline{X}(iy_2)] \underline{P} \underline{E}^{-1/2}. \quad (17)$$

Then, Eqs. (9) and (15) give

$$\underline{A} = \underline{Q} \underline{Z} \underline{Q}^T, \quad (18)$$

where $\underline{Z}(iy_1, iy_2)$ is a diagonal matrix given by

$$[\underline{Z}]_{mn} = \delta_{mn} \frac{y_1^2 + \omega_m^2}{y_2^2 + \omega_m^2}. \quad (19)$$

The second step is to diagonalize \underline{A} , since Eq. (17) states that the eigenvectors of \underline{A} give the orthogonal matrix $\underline{Q}(iy_1, iy_2)$ and the eigenvalues give $(y_1^2 + \omega_m^2)/(y_2^2 + \omega_m^2)$, and therefore, ω_m . The final step is to calculate \underline{N} , the matrix elements of the density operator. From Eqs. (9) and (15),

$$\underline{N} = [\underline{Y}(iy_1)]^{-1/2} \underline{Q}^T \underline{E}^{1/2} \underline{P}^T. \quad (20)$$

Now, from ω_m and \underline{N} , $\chi(\mathbf{r}, \mathbf{r}'; z)$ is given directly by Eq. (3).

$$\chi(\mathbf{r}_1, \mathbf{r}_2; E) = \chi^0(\mathbf{r}_1, \mathbf{r}_2; E) + \int d\mathbf{r}_3 \int d\mathbf{r}_4 \chi^0(\mathbf{r}_1, \mathbf{r}_3; E) K(\mathbf{r}_3, \mathbf{r}_4) \chi(\mathbf{r}_4, \mathbf{r}_2; E). \quad (21)$$

Here, χ^0 is the density-density response function of the hypothetical independent particles in the Kohn-Sham formalism, and $K(\mathbf{r}, \mathbf{r}')$ is the kernel given by

$$K(\mathbf{r}, \mathbf{r}') = \frac{2}{|\mathbf{r} - \mathbf{r}'|} + \frac{dV_{xc}}{d\rho} \delta(\mathbf{r} - \mathbf{r}'), \quad (22)$$

in Rydberg units, which will be used throughout the paper. V_{xc} is the exchange-correlation potential in the LDA. In the present work, Wigner's interpolation formula²⁰ for the correlation energy will be used. The LDA retarded one-particle Green's function is given as

$$G(\mathbf{r}, \mathbf{r}'; E) = \sum_i \frac{\phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}')}{E - \epsilon_i + i\delta}, \quad (23)$$

where ϕ_i and ϵ_i are, respectively the wave functions and eigenvalues of the self-consistent Kohn-Sham equations. Then, χ^0 can be written as¹⁵

$$\chi^0(\mathbf{r}, \mathbf{r}'; E) = \sum_i^{\text{occ}} [\phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}') G(\mathbf{r}, \mathbf{r}'; \epsilon_i + E) + \phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}') G^*(\mathbf{r}, \mathbf{r}'; \epsilon_i - E)]. \quad (24)$$

Since we adopt the jellium-sphere background model, G is given as the product of spherical Bessel-type and Hankel-type solutions of the Schrödinger equation with the LDA effective potential.

The formalism presented in Sec. II is applied to the TDLDA χ for sodium clusters. The positive ion cores are replaced by the jellium sphere with the density taken to be the same as the valence electrons in bulk sodium. (The Wigner-Seitz radius r_s is set to be 4 a.u.) All the sodium clusters to be studied (Na_2 , Na_8 , Na_{18} , Na_{20} , Na_{34} , and Na_{40}) have closed-shell electronic structure and the jellium-sphere background model is expected to give a good representation of their electronic structures. In the next section, we will give the results for the imaginary part of the dynamical dipole polarizabilities calculated from the χ as

$$\alpha(\omega) = - \int d\mathbf{r} \int d\mathbf{r}' z \chi(\mathbf{r}, \mathbf{r}'; \omega) z'. \quad (25)$$

The calculated ω_m and \underline{N} depend on y_1 and y_2 . Hence, the reasonable choices of y_1 and y_2 are important in the actual calculation. This point will be discussed further in Sec. III. The y_1 and y_2 dependences of the energies of the important excitations, that is, the collective modes are found to be weak.

III. APPLICATION TO SODIUM CLUSTERS

A. TDLDA formalism

In the TDLDA, the density-density response function χ satisfies^{14, 15, 18, 19}

The imaginary part of $\alpha(\omega)$ has poles at the excitation energies of the system and gives $\sigma(\omega)$, the photoabsorption cross section of sodium clusters:¹⁵

$$\sigma(\omega) = 4\pi \frac{\omega}{c} \text{Im}\alpha(\omega), \quad (26)$$

which can be compared to the experiments.¹²

The static response function of the system $\chi(0)$ is a ground-state property and is expected to be described well in the LDA. Hence, a small value for y_1 (0.01 Ry) is used in the present work. [Equation (24) cannot be used for an exactly zero energy, because $G(\mathbf{r}, \mathbf{r}'; \epsilon_i)$ is singular.] As can be seen from Eq. (19), all the eigenvalues of \underline{A} are nearly degenerate (close to 1) if $y_1 \approx y_2$. Hence, y_2 should be considerably larger than y_1 . On the other hand, if the choice for y_2 is too large, similar eigenvalues are found close to zero. (Since $0 < y_1 < y_2$, all the eigenvalues of \underline{A} are between 0 and 1.) Therefore, y_2 should be comparable with the excitation energies of interest. The classical surface dipole resonance (surface plasmon) energy, ω_s^{cl} , is 0.25 Ry for the metallic sphere with $r_s = 4$. This is independent of the cluster size. The experimental value ω_s^{expt} is found to have a similar magnitude but to be red-shifted compared with ω_s^{cl} .¹² (The origin of the shift is considered to be the surface diffuseness of the electron density.) Other single-particle-hole pair excitations are also expected to be in the same energy region. Therefore, $y_2 = 0.5$ Ry is used in the present work.

Since the systems studied have spherical symmetry, we can utilize spherical harmonics and only the radial part of the wave functions has to be solved for numerically on a discrete grid within the LDA self-consistent calculation. These discrete points on r are used as the sites in the present matrix formalism. In this work, uniform grids with distances of 0.2 (a.u.) between grid points are used. The maximum points on r are determined as the points beyond which the LDA effective potentials are less than 10^{-3} Ry, unless otherwise specified. Furthermore, the $\text{Im}\alpha(\omega)$ for ω with a small imaginary part ($\text{Im}\omega = 0.001$ Ry) are calculated in order to give finite widths to the δ functions and to display their oscillator strengths clearly.

B. Results

Here, the TDLDA $\text{Im}\alpha(\omega)$ for Na_N ($N=2, 8, 18, 20, 34,$ and 40) normalized by the classical static dipole polarizability R^3 is given (R is the radius of the jellium sphere). In Fig. 1, $\text{Im}\alpha(\omega)$ for Na_2 given by the full TDLDA calculation along the real energy axis is shown together with the LDA $\text{Im}\alpha^0(\omega)$, that is, χ^0 instead of χ is used in Eq. (25). Within the LDA and the jellium-sphere background model, the Na_2 cluster is in a simple electronic configuration; $1s^2$. Since the lowest-unoccupied state is $1p$, the LDA independent-particle response function χ^0 has a pole at $\epsilon_{1s} - \epsilon_{1p} = 0.15$ Ry. The higher excitations constitute a continuum spectrum above the TDLDA ionization energy, that is, the absolute value of the LDA highest-occupied-state energy $|\epsilon_{1s}| = 0.25$ Ry.

As can be seen from the TDLDA results, the pole in the renormalized response function χ is found at a higher energy (0.19 Ry) than χ^0 because of the electron-electron interaction given by $K(\mathbf{r}, \mathbf{r}')$. Hence, the new pole with a large oscillator strength in the TDLDA is considered to be the collective mode of two valence electrons corresponding to the classical surface plasmon, and therefore is denoted by ω_s . Since ω_s is found to be still lower than the ionization potential, there is no Landau damping for the ω_s in Na_2 . Hence, the finite width of the peak at ω_s is due only to the externally introduced $\text{Im}\omega$.

In Fig. 2, $\text{Im}\alpha(\omega)$ calculated from the present formalism with two different numbers of excitations is given. The numbers of excitations, or, the numbers of sites used are 110 and 142, which give the maximum points on r beyond which the LDA effective potentials are less than 10^{-3} and 10^{-4} (Ry), respectively. In both cases, the position as well as the oscillator strength of the collective mode is very close to the full TDLDA result. The number of sites in the actual calculation is finite in the present

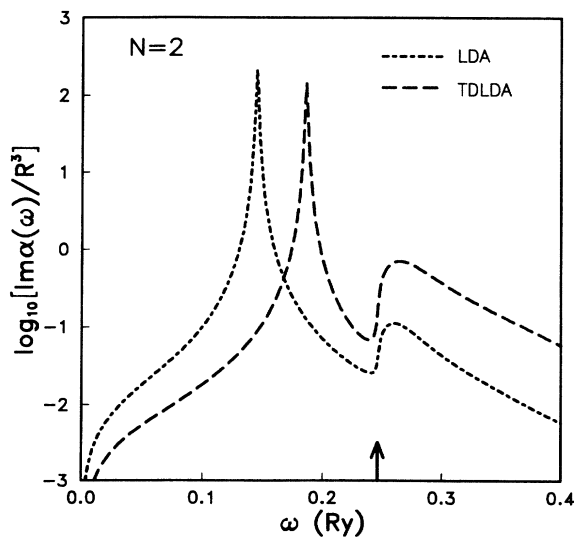


FIG. 1. $\text{Im}\alpha(\omega)$ for Na_2 given through the LDA χ^0 and the TDLDA χ . Calculations are performed on the line above the real-energy axis ($\text{Im}\omega = 0.001$ Ry). The ionization energy $|\epsilon_{1s}|$ is indicated by an arrow.

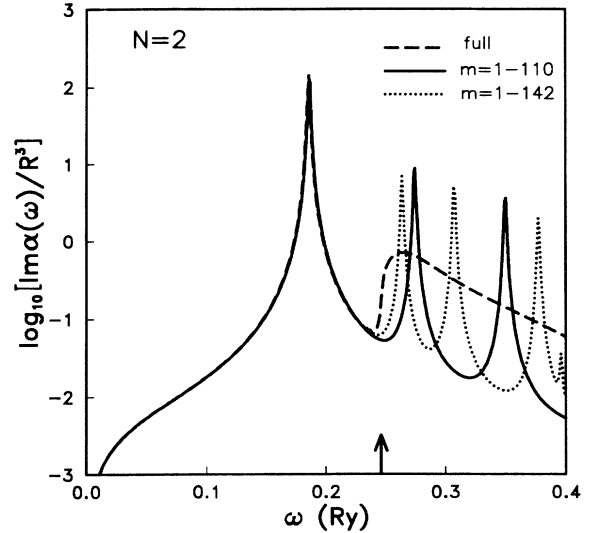


FIG. 2. TDLDA $\text{Im}\alpha(\omega)$ for Na_2 given by the present formalism with two different numbers of excitations (ω_m), 110 and 142, together with the full-calculation results along the real-energy axis. The arrow indicates the ionization energy.

formalism, and the discrete spectrum is given above the ionization potential as well as below it. Figure 2 shows that the larger-area calculation gives more excitations in the continuum-spectrum region with smaller oscillator strength on each excitation in better accord with the full TDLDA-calculated spectrum.

In the case of larger clusters, the electronic structure is more complicated and the excitation spectra have a richer structure than the Na_2 . Figure 3(a) shows $\text{Im}\alpha(\omega)$ for Na_8 . The present formalism still gives the plasma resonance energy ω_s and its oscillator strength fairly well, although some poles (or resonant excitations above the ionization energy $|\epsilon_{1p}| = 0.25$ Ry) are missing.

To see the y_1 and y_2 dependences of the excitation energies in the present formalism, several different sets of y_1 and y_2 are used for Na_8 : $(y_1, y_2) = (0.01, 0.3), (0.01, 0.1), (0.1, 0.5),$ and $(0.001, 0.5)$ (Ry). Their results are shown in Figs. 3(b) and 3(c) along with the result of the standard choice for (y_1, y_2) . Figure 3(b) shows that the y_1 dependence of the excitation spectrum is very weak and $y_1 = 0.01$ Ry and $y_1 = 0.001$ Ry give almost the identical results. The spectrum is found to have a little y_2 dependence in its higher energy region [Fig. 3(c)]. The important plasma resonance energy ω_s shows a very weak y_2 dependence if y_2 is within a reasonable range.

In Fig. 4, results for $\text{Na}_{18}, \text{Na}_{20}, \text{Na}_{34},$ and Na_{40} are given. Although ω_s and its strength in Na_{40} given by the present formalism show a little deviation from those given by the full calculation along the real-energy axis, in $\text{Na}_{18}, \text{Na}_{20},$ and Na_{34} the present formalism gives the plasma resonance energies and their strengths which are very close to the results by the full-real-axis calculations.

IV. DISCUSSION

As can be seen from the definition (1), the density-density response function χ denotes a specific two-

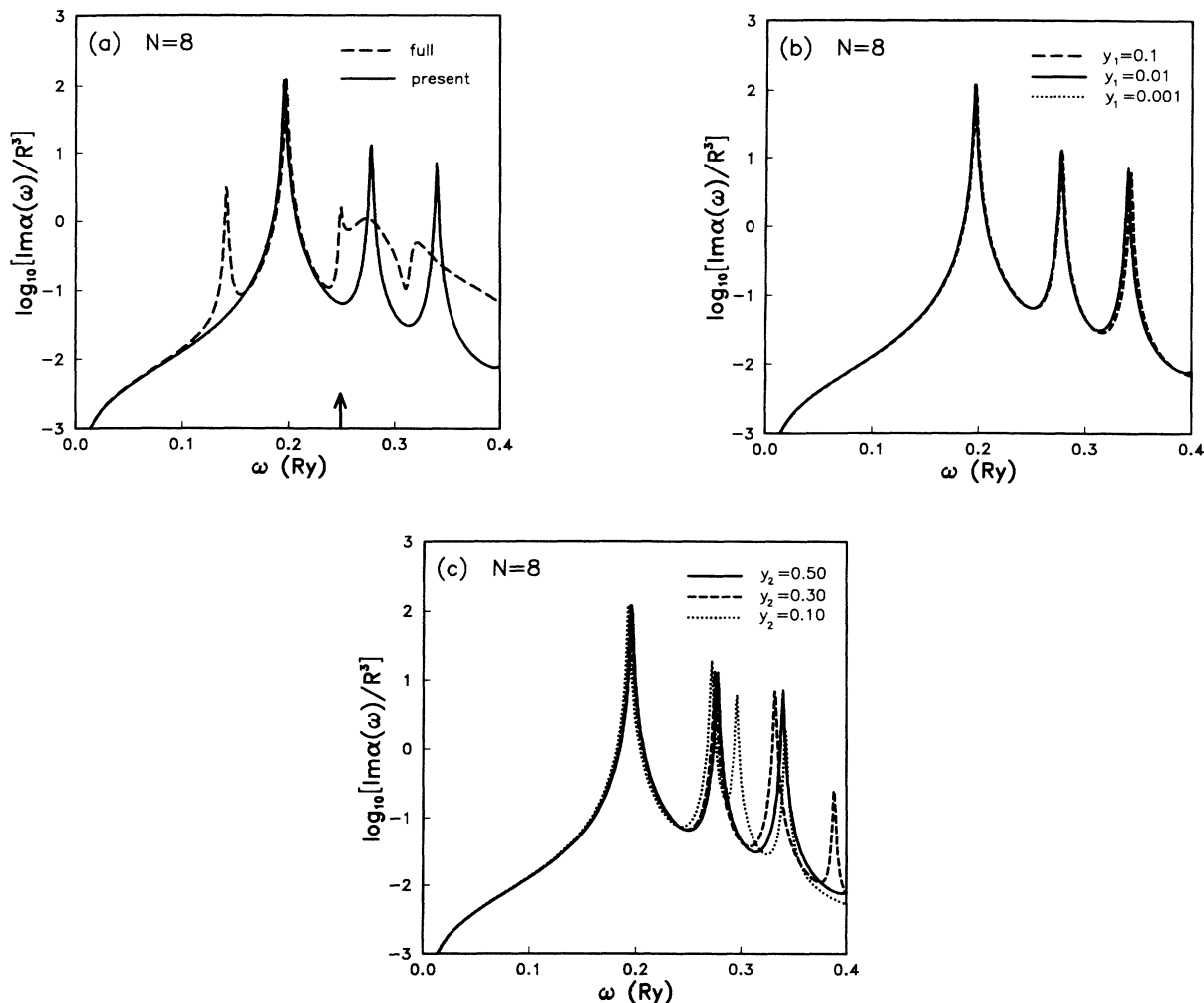


FIG. 3. TDLDA $\text{Im}\alpha(\omega)$ for Na_8 . (a) Results given by the present formalism (solid line) and by the full calculation along the real-energy axis (dashed line). In the present-formalism calculation, the standard values of y_1 and y_2 (0.01 and 0.5 Ry, respectively) are used. The arrow indicates the ionization energy. (b) Results given by the present formalism with three different y_1 values, 0.1, 0.01, and 0.001 Ry (y_2 is fixed at 0.5 Ry). Results with $y_1 = 0.01$ and 0.001 Ry are almost identical and the difference does not show up in this figure. (c) Results given by the present formalism with three different y_2 values, 0.5, 0.3, and 0.1 Ry (y_1 is fixed at 0.01 Ry).

particle Green's function. Finite- (nonzero-) temperature Green's-function theory tells us that a knowledge of χ on an infinite number of points on the imaginary axis, *in principle*, gives the *unique* analytic continuation of χ on the upper-half plane. However, it is not straightforward to do the analytic continuation in the calculation for real systems. In the present work, we have given an approximate way to describe the behavior of $\chi(\mathbf{r}, \mathbf{r}'; z)$ from χ on two points on the imaginary axis. By restricting the number of excitations to the number of sites, excitation energies and their strengths, which give the explicit form of $\chi(\mathbf{r}, \mathbf{r}'; z)$, are determined from the values of $\chi(\mathbf{r}, \mathbf{r}'; iy_1)$ and $\chi(\mathbf{r}, \mathbf{r}'; iy_2)$ with *linear algebraic calculation*. If more excitations were assumed, χ on more than two points would be necessary to determine the excitation energies

and their strengths. In that case, however, we have to solve a *nonlinear* optimization problem, which still needs further manipulations and is beyond the scope of this paper.

The excitation energies and their strengths given by the present theory have been compared with the results by the full calculation along the real-energy axis. And the comparison has revealed that the present formalism gives the collective excitation energies and their strengths very well. Since the formalism can be combined with any approximation for calculating the density-density response function, one of the advantages of the present method is that we can estimate the energies and the strengths of the important collective excitations from $\chi(\mathbf{r}, \mathbf{r}'; z)$ on only two different energy points. Without this approach, it is

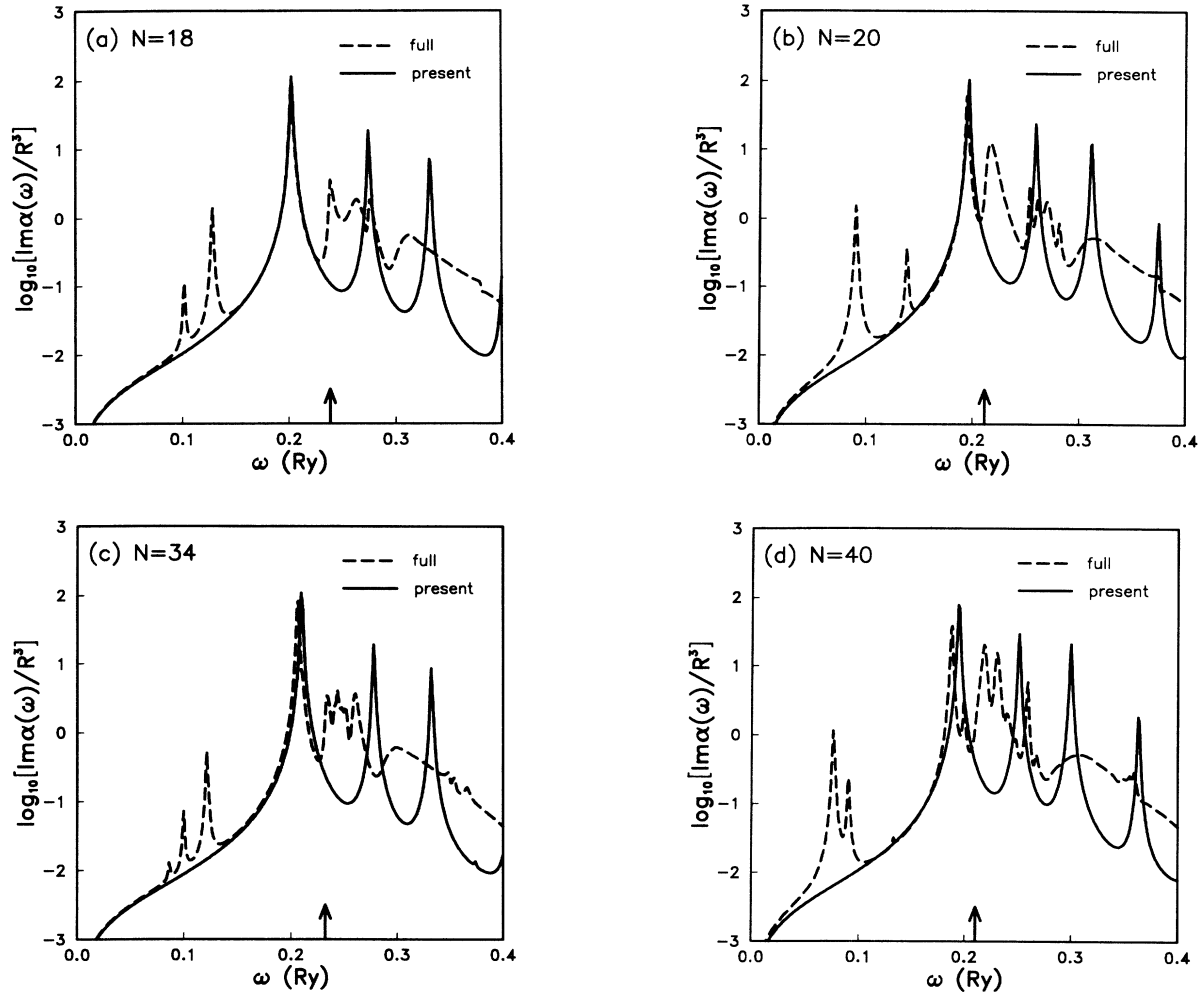


FIG. 4. TDLDA $\text{Im}\alpha(\omega)$ for (a) Na_{18} , (b) Na_{20} , (c) Na_{34} , and (d) Na_{40} . Solid lines represent the results by the present formalism, and dashed lines are the full-calculation results along the real-energy axis.

necessary to calculate χ on a large number of points along the real-energy axis. Therefore, the present formalism is especially useful in cases where the approximation for χ to be used is too time consuming to evaluate.

In addition to the behavior around the collective excitations, the present $\chi(\mathbf{r}, \mathbf{r}'; z)$ describes the behavior around $z = iy_1$ and iy_2 fairly well. In the present work, we have used a very small y_1 giving a good static limit ($z \rightarrow 0$) for χ . In that case, $\sigma(\omega)$ given by the present formalism through Eq. (26) satisfies the following sum rule¹⁵ with sufficient accuracy:

$$\int_0^\infty \frac{\sigma(\omega)}{\omega^2} d\omega = \frac{2\pi^2}{c} a(0), \quad (27)$$

where $a(0)$ is given from $\chi(\mathbf{r}, \mathbf{r}'; 0)$ evaluated directly using Eq. (21). Equation (27) is equivalent to the usual Kramers-Kronig relation between $\text{Re}\alpha(0)$ and $\text{Im}\alpha(\omega)$.

In the standard perturbative (diagrammatic) many-body theory, the time-ordered density-density response function χ^{TO} gives the screened Coulomb interaction propagator W as

$$W(\mathbf{r}_1, \mathbf{r}_2; E) = v(\mathbf{r}_1, \mathbf{r}_2) + \int d\mathbf{r}_3 \int d\mathbf{r}_4 v(\mathbf{r}_1, \mathbf{r}_3) \chi^{\text{TO}}(\mathbf{r}_3, \mathbf{r}_4; E) v(\mathbf{r}_4, \mathbf{r}_2), \quad (28)$$

where v is the bare Coulomb interaction. χ^{TO} is related to the retarded χ as

$$\begin{aligned} \text{Re}\chi^{\text{TO}}(\mathbf{r}, \mathbf{r}'; E) &= \text{Re}\chi(\mathbf{r}, \mathbf{r}'; E), \\ \text{Im}\chi^{\text{TO}}(\mathbf{r}, \mathbf{r}'; E) &= \text{sgn}(E) \text{Im}\chi(\mathbf{r}, \mathbf{r}'; E). \end{aligned} \quad (29)$$

Therefore, the present formalism gives a useful expression for W through Eqs. (28) and (29). The representative poles in W given by the present formalism enable us to use contour integration which is a powerful technique in the diagrammatic theory. For example, the self-energy of

the electrons in the GW approximation of Hedin is given by

$$\Sigma(\mathbf{r}, \mathbf{r}'; E) = \int_{-\infty}^{\infty} \frac{dz}{2\pi i} e^{-i\delta z} G^{GW}(\mathbf{r}, \mathbf{r}'; E - z) W(\mathbf{r}, \mathbf{r}'; z), \quad (30)$$

where G^{GW} is the time-ordered one-electron Green's function in the GW approximation. The evaluation of Σ using the contour-integration technique with finite number of poles is straightforward.⁸ On the other hand, the continuum excitation spectrum given by the full calculation along the real-energy axis does not give us an easy way to evaluate Σ .

The application of the present formalism to extended systems is an interesting problem. The formalism in Fourier space has been done and will be discussed elsewhere.²¹

V. SUMMARY AND CONCLUSION

In this work, we have presented a new formalism to approximate the excitation spectrum of interacting many-body systems from the density-density response function on two pure imaginary-energy points. The basic approximation used is to restrict the number of the excitations to the number of sites in the real-space grid considered. The new method has been applied to the valence electrons in sodium clusters in the TDLDA with a jellium-sphere background model. The results show that the present formalism gives fairly accurate collective-mode energies and their oscillator strengths compared to the full calcu-

lation along the real-energy axis, which is much more time consuming. Since the present formalism can be applied not only to the TDLDA but also to *any* approximations for the density-density response functions, the formalism will be especially powerful in predicting collective excitations of systems where the full calculation in the desired approximation is impossible. Moreover, in some applications, the approximate excitation spectra obtained by the present formalism are more useful in the diagrammatic theory than the continuum spectra given by the full calculation.

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