

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

IC/89/228
INTERNAL REPORT
(Limited distribution)

International Atomic Energy Agency
and
United Nations Educational Scientific and Cultural Organization
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

ON THE DYNAMIC POLARIZABILITY OF ATOMS *

K. Nuroh **

International Centre for Theoretical Physics, Trieste, Italy,

and

E. Zaremba

Department of Physics, Queen's University, Kingston, Ontario K7L 3N6, Canada.

ABSTRACT

The positive frequency dependent polarizability of atoms is discussed in terms of the particle-hole polarization propagator. It is considered in the simplest approximation defined by the Bethe-salpeter equation which includes a subset of particle-hole interactions to all orders in the Coulomb potential. Its solution is used to show the relationship between different formulations of atomic photoabsorption via the effective dipole matrix element (Fermi's 'golden rule'), the TD LDA and the reaction matrix.

1. INTRODUCTION

The dynamic dipolar polarizability, $\alpha(\omega)$, is the central quantity in the calculation of photoabsorption spectra of atoms. Various techniques and approximations have been used in its determination, starting from simple independent particle models ¹⁾⁻³⁾ and progressing to ever more sophisticated many-body descriptions ⁴⁾⁻¹⁶⁾. These studies have amply demonstrated the importance of collective behaviour in the response of atoms to external time-dependent perturbations.

One of the most useful concepts in a many-body description is the notion of a self-consistent field. The polarization of the atom by the external field gives rise to an induced electrostatic potential which in turn affects the dynamics of the atomic electrons. In this way the induced potential includes approximately the effects of electron-electron interactions. Such a picture forms the basis of the so-called random phase approximation (RPA), first introduced in the context of the interacting electron gas ¹⁷⁾. Of course not all many-body effects can be represented in this way; for example the antisymmetry of the many-electron wave function requires a generalization to non-local effective potentials as in the RPA plus exchange (RPAE) ¹¹⁾. The latter is also referred to as the linearized time-dependent Hartree-Fock approximation (TDHF) and presumably provides a more accurate description of the atomic response than the RPA.

More recently, a time-dependent generalization of density functional theory has been used to calculate atomic photoabsorption (TD LDA). Although identical in spirit to the RPA, its use of a local self-consistent potential leads to a number of simplifications. This approach has produced surprisingly accurate cross-sections above ionization thresholds ^{14),15)} and are in substantial agreement with RPAE calculations.

Our objective in this paper is to make a formal comparison of the various theoretical formulations of photoabsorption, all of which have a self-consistent field as a common element. To emphasize the similarities we begin from a general field-theoretic point of view in which the particle-hole propagator appears as the central quantity. We then consider its calculation in the simplest approximation defined by the Bethe-Salpeter equation which includes a subset of particle-hole interactions to all orders in the Coulomb potential. It is shown how the solution of this equation can be formulated in terms of an effective dipole matrix element, thereby making contact with the work of Amusia ¹¹⁾ and Wendin ¹⁶⁾. Finally, recasting these equations into a real-space form makes apparent their relationship to the TD LDA formulation.

* To be submitted for publication.

** Present address: Nipissing University College, North Bay, Ontario P1B 8L7, Canada.

2. FORMULATION

The photoabsorption cross-section $\sigma(\omega)$ for an atom is related to its dynamic dipolar polarizability according to the formula

$$\sigma(\omega) = \frac{4\pi}{c} \omega \text{Im}\alpha(\omega) \quad (2.1)$$

In what follows, we employ atomic units ($e^2 = m_e = \hbar = 1$). The dynamic polarizability $\alpha(\omega)$ can in turn be expressed as

$$\alpha(\omega) = \iint d\vec{r} d\vec{r}' z z' \chi(\vec{r}, \vec{r}', \omega) \quad (2.2)$$

where $\chi(\vec{r}, \vec{r}', \omega)$ is the Fourier transform of the retarded density-density response function

$$\chi(\vec{r}, \vec{r}', t) = i\theta(t) \langle 0 | [n(\vec{r}, t), n(\vec{r}', 0)] | 0 \rangle \quad (2.3)$$

In Eq.(2.3) above, $|0\rangle$ is the exact N-particle ground state and the square brackets denote the commutator of the two Heisenberg density operators. The factor $\theta(t)$ is the Heaviside unit step function.

Introducing the total dipole moment operator

$$d_z = \int d\vec{r} z n(\vec{r}) \quad (2.4)$$

$\alpha(\omega)$ may be expressed as

$$\alpha(\omega) = i \int_0^\infty dt e^{i\omega t} \langle 0 | [d_z(t), d_z] | 0 \rangle \quad (2.5)$$

To proceed further we use a second quantized representation of the dipole operator d_z according to the prescription

$$d_z = \sum_{\lambda\mu} \langle \mu | z | \lambda \rangle C_\mu^\dagger C_\lambda \equiv \sum_{\lambda\mu} d_{\mu\lambda} C_\mu^\dagger C_\lambda \quad (2.6)$$

where the summation is over a complete set of single particle states, including spin. For the moment we leave these states unspecified. The expectation value in (2.5) now becomes

$$\langle 0 | [d_z(t), d_z] | 0 \rangle = \sum_{\alpha\beta} d_{\mu\lambda} d_{\alpha\beta} \langle 0 | [C_\mu^\dagger(t) C_\lambda(t), C_\alpha^\dagger C_\beta] | 0 \rangle \quad (2.7)$$

Thus the calculation of $\alpha(\omega)$ requires knowledge of the particle-hole propagator in (2.7). Its evaluation is conveniently carried out using a graphical analysis of the time-ordered propagator Π (18)

$$\Pi_{\lambda\mu;\alpha\beta}(t) = i \langle 0 | T [C_\mu^\dagger(t) C_\lambda(t) C_\alpha^\dagger C_\beta] | 0 \rangle \quad (2.8)$$

The time Fourier transform of (2.8) has the Lehmann representation

$$\Pi_{\lambda\mu;\alpha\beta}(\omega) = \sum_n \left[\frac{\langle 0 | C_\mu^\dagger C_\lambda | n \rangle \langle n | C_\alpha^\dagger C_\beta | 0 \rangle}{\omega_n - \omega_0 - \omega - i\delta} + \frac{\langle 0 | C_\alpha^\dagger C_\beta | n \rangle \langle n | C_\mu^\dagger C_\lambda | 0 \rangle}{\omega_n - \omega_0 + \omega - i\delta} \right] \quad (2.9)$$

A comparison of (2.9) with the Lehmann representation of (2.7) shows that $\alpha(\omega)$ can finally be expressed as

$$\alpha(\omega) = \sum_{\alpha\beta} d_{\mu\lambda} d_{\alpha\beta} \Pi_{\lambda\mu;\alpha\beta}(\omega) \quad (2.10)$$

which is valid for positive frequencies.

The dynamic polarizability given by Eq.(2.10) is exact. All the many-body aspects such as exchange and electron correlation effects are buried in Π and, to some extent, in the single particle basis. For example, the Hartree-Fock approximation generates a basis in which the orbitals are determined by a non-local self-consistent field. Such a basis is particularly convenient since as shown in Ref.18, the interacting part of the many-body Hamiltonian can then be written in normal ordered form which simplifies the systematic perturbation expansion of Π . This expansion leads to the following general equation defining the particle-hole propagator

$$\Pi_{\lambda\mu;\alpha\beta}(\omega) = \Pi_{\lambda\mu;\alpha\beta}^0(\omega) + \sum_{\rho\sigma} \Pi_{\lambda\mu;\rho\sigma}^0(\omega) \Gamma_{\rho\sigma;\eta\nu}(\omega) \Pi_{\eta\nu;\alpha\beta}(\omega) \quad (2.11)$$

Here Γ is an effective particle-hole interaction while Π^0 represents the propagator for an independent particle and hole. The most commonly used approximation for the calculation of Π is provided by the Bethe-Salpeter equation

$$\Pi_{\lambda\mu;\alpha\beta}(\omega) = \Pi_{\lambda\mu;\alpha\beta}^0(\omega) + \sum_{\rho\sigma} \Pi_{\lambda\mu;\rho\sigma}^0(\omega) \Gamma_{\rho\sigma;\eta\nu} \Pi_{\eta\nu;\alpha\beta}(\omega) \quad (2.12)$$

The lowest order propagator Π^0 is given by

$$i\Gamma_{\lambda\mu;\alpha\beta}^0(\omega) = \delta_{\lambda\alpha}\delta_{\mu\beta} \left[\frac{\psi(\alpha-F)\psi(F-\beta)}{\omega_{\alpha\beta} - \omega - i\delta} + \frac{\psi(F-\alpha)\psi(\beta-F)}{\omega_{\beta\alpha} + \omega - i\delta} \right] \quad (2.13)$$

with

$$\omega_{\alpha\beta} = \omega_\alpha - \omega_\beta > 0 \quad \text{if} \quad \alpha > F, \quad \beta < F \quad (2.14)$$

In Eq.(2.13), F denotes the Fermi level separating filled and empty states. The lowest order particle-hole interaction in Eq.(2.12) is independent of ω and is given by

$$\Gamma_{\rho\sigma;\eta\nu}^0 = \langle \rho\nu | v | \sigma\eta \rangle - \langle \nu\rho | v | \sigma\eta \rangle \quad (2.15)$$

with

$$\langle \rho\nu | v | \sigma\eta \rangle = \iint d\vec{r} d\vec{r}' \frac{\psi_\rho^*(\vec{r})\psi_\sigma(\vec{r})\psi_\nu^*(\vec{r}')\psi_\eta(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad (2.16)$$

The first term in Eq.(2.15) is referred to as the direct Coulomb matrix element while the second is the exchange counterpart. These terms are represented by the Feynman diagrams in Fig.1. Iteration of (2.12) shows that the Bethe-Salpeter equation takes into account the pair interaction (2.15) to all orders.

3. EFFECTIVE DIPOLE MATRIX ELEMENT

In this section we obtain a compact expression for $\alpha(\omega)$ in terms of an effective dipole matrix element which has been used extensively in earlier analyses of the photoabsorption cross section.

Denoting a pair state ($\alpha\beta$) by the index n , Eq.(2.10) may be written as

$$\alpha(\omega) = \sum_{nn'} d_n \Pi_{nn'}^0(\omega) d_{n'} \quad (3.1)$$

Here we assume for convenience that the basis states are real so that $d_n^* = d_n$. This assumption is not essential since each state in the complete set has a time-reversed pair at the same energy.

We now define the effective dipole matrix element through the equation

$$D_n(\omega) = d_n - \sum_{nn'} \Gamma_{nn'}^0 \Pi_{nn'}^0(\omega) D_{n'}(\omega) \quad (3.2)$$

where we have used the fact that Π^0 is diagonal: $\Pi_{nn'}^0 = \delta_{nn'} \Pi_n^0$. With this definition $\alpha(\omega)$ can be expressed as

$$\alpha(\omega) = \sum_n d_n \Pi_n^0(\omega) D_n(\omega) \quad (3.3)$$

If we consider excitations to the continuum, the imaginary part of (3.3) can be expressed in a particularly suggestive form. We have

$$\begin{aligned} \text{Im } \alpha(\omega) &= \sum_n \frac{1}{2i} \left[d_n \Pi_n^0 D_n + d_n \Pi_n^{0*} D_n^* \right] \\ &= \sum_n \frac{1}{2i} \left[(D_n^* - \sum_{nn'} \Gamma_{nn'}^0 \Pi_{nn'}^{0*} D_n^*) \Pi_n^0 D_n \right. \\ &\quad \left. - (D_n + \sum_{nn'} \Gamma_{nn'}^0 \Pi_{nn'}^0 D_n) \Pi_n^{0*} D_n^* \right] \\ &= \sum_n \frac{1}{2i} \left[D_n^* (\Pi_n^0 - \Pi_n^{0*}) D_n \right] \\ &= \sum_n |D_n(\omega)|^2 \text{Im } \Pi_n^0(\omega) \end{aligned} \quad (3.4)$$

Reverting to the particle-hole notation ($\alpha\beta$) and using (2.13), we finally obtain (for $\omega > 0$)

$$\text{Im } \alpha(\omega) = \pi \sum_{\substack{\alpha>F \\ \beta<F}} |D_{\alpha\beta}(\omega)|^2 \delta(\omega - \omega_{\alpha\beta}) \quad (3.5)$$

This result is the same as obtained using time-dependent perturbation theory for independent particles, but with the dipole operator d_z replaced by a complex effective dipole operator $D_z(\omega)$. It should be emphasized that the result (3.5) is not general but is dependent on the fact that Γ is real, as in the HF approximation. This assumption has the consequence that ionization thresholds occur at the unperturbed excitation energies.

Eq.(3.5) is not applicable for discrete transitions however; in this case one must revert to (3.2) to extract the singular contribution from the equation. A singularity at the frequency $\omega = \bar{\omega}$ implies that $D_n(\omega)$ behaves as

$$D_n(\omega) \sim \frac{R_n}{\omega - \bar{\omega} - i\delta} \quad (3.6)$$

where R_n is the residue at this frequency. Multiplying Eq.(3.2) through by the resonant denominator and taking the limit $\omega \rightarrow \bar{\omega}$, one finds the homogeneous equation

$$R_n = - \sum_{n'} \Gamma_{nn'}^0 \Pi_{n'}^0(\bar{\omega}) R_{n'} \quad (3.7)$$

This equation has non-trivial solutions only for certain frequencies which define the excitation energies of the interacting system. Once the resonant frequencies have been determined, the residues can be found from the equation

$$\sum_{n'} \Gamma_{nn'}^0 \frac{d\Pi_{n'}^0(\bar{\omega})}{d\bar{\omega}} R_{n'} = + d_n \quad (3.8)$$

and the absorptive part of the polarizability is

$$\text{Im } \alpha(\omega) = \pi \sum_n d_n \Pi_n^0(\bar{\omega}) R_n \delta(\omega - \bar{\omega}) \quad (3.9)$$

There of course is a contribution of this kind from each of the resonant frequencies.

4. GRAPHICAL ANALYSIS OF $\text{Im}\alpha(\omega)$

We next make contact with some earlier work of Wendin. Iteration of Eqs.(3.3) and (3.2) generates the series

$$\alpha(\omega) = \left\{ \sum_n d_n \Pi_n^0(\omega) d_n - \sum_{nn'} d_n \Pi_n^0(\omega) \Gamma_{nn'}^0 \Pi_{n'}^0(\omega) d_{n'} + \dots \right\} \quad (4.1)$$

The contribution to $\alpha(\omega)$ from various orders in Γ^0 may be represented graphically as follows: we denote a dipole matrix element by a dot (\bullet), an interaction vertex by a cross (\times) and the particle-hole propagator by a labelled line (---_n). As an example, the first order contribution

$$\alpha^{(1)}(\omega) = - d_n \Pi_n^0(\omega) \Gamma_{nn'}^0 \Pi_{n'}^0(\omega) d_{n'} \quad (4.2)$$

is shown in Fig.2. In Eq.(4.2) and the following, it is convenient to make use of a repeated index summation convention. Since we are interested in $\text{Im}\alpha(\pi)$, we express Π_n^0 in terms of its real and imaginary parts

$$\Pi_n^0(\omega) = R_n^0(\omega) + i I_n^0(\omega) \quad (4.3)$$

The imaginary part of (4.2) is then

$$\text{Im } \alpha^{(1)}(\omega) = -d_n R_n^0 \Gamma_{nn'}^0 I_{n'}^0 d_{n'} - d_n I_n^0 \Gamma_{nn'}^0 R_{n'}^0 d_{n'} \quad (4.4)$$

The two terms in (4.4) are in fact equal since $\Gamma_{nn'}^0 = \Gamma_{n'n}^0$. Eq.(4.4) is represented graphically in Fig.3 where we follow the notation of Ref.19.

A single bar through a particle-hole propagator denotes the real part of Π^0 while a double bar denotes the imaginary part. Each term in the expansion of $\text{Im } \alpha(\omega)$ can be grouped according to how many times a double bar appears; it must of course be an odd number for the graph to be imaginary, i.e. $I_n^0(\omega)$ appears $(2m+1)$ times. A few examples will illustrate the general structure.

(2) $m = 0$ graphs: I^0 appearing once

The lowest order contribution is $d_n I_n^0 d_n$ (Fig.4). However, expressions like (4.4) also contribute to the $m = 0$ graphs since each contains a single imaginary propagator. It is clear that all graphs of this type are generated by an arbitrary number of real insertions which can be summed by defining the polarization function

$$P_n = d_n - \Gamma_{nn'}^0 R_{n'}^0, P_{n'} = d_{n'} - P_{n'} R_{n'}^0 \Gamma_{n'n}^0 \quad (4.5)$$

The sum of all $m = 0$ graphs is therefore $P_n I_n^0 P_n$ which is represented in Fig.5. A circle around a dot will denote the effective dipole matrix element defined in Eq.(4.5).

(b) $m = 1$ graphs: I^0 appearing thrice

The basic term is $d_n I_n^0 \Gamma_{nn'}^0 I_{n'}^0 \Gamma_{n'n}^0 I_n^0 d_n$ illustrated in Fig.6. The factors d_n can be replaced by P_n to sum up all real propagator insertions between d_n and I_n^0 . Similar insertions between adjacent I_n^0 factors can be summed by replacing $\Gamma_{nn'}^0$ by the effective interaction

$$\Gamma_{nn'}^0(\omega) = \Gamma_{nn'}^0 - \Gamma_{nn''}^0 R_{n''}^0(\omega) \Gamma_{n''n'}^0(\omega) \quad (4.6)$$

Since $\Gamma_{nn'}^0$ is symmetric, $\Gamma_{nn''}^0$ is as well. Thus the sum of all $m = 1$ graphs is given by $P_n I_n^0 \Gamma_{nn'}^0 I_{n'}^0 \Gamma_{n'n}^0 I_n^0 P_n$ which is illustrated in Fig.7. The circle around a cross denotes the effective pair interaction in Eq.(4.6).

We finally obtain

$$\begin{aligned} \text{Im } \alpha(\omega) &= P_n I_n^0 P_n - P_n I_n^0 \Gamma_{nn} I_n^0 \Gamma_{n'n''} I_n^0 P_{n''} + \dots \\ &= D_n^s(\omega) I_n^0(\omega) D_n(\omega) \end{aligned} \quad (4.7)$$

where we note that

$$\begin{aligned} D_n(\omega) &= P_n(\omega) - i \Gamma_{nn}(\omega) I_n^0(\omega) D_n(\omega) \\ &= d_n - \Gamma_{nn}^0 I_n^0(\omega) D_n(\omega) \end{aligned} \quad (4.8)$$

This approach therefore leads to the same result, Eq.(3.4) obtained earlier. From Eq.(2.13) we see that for $\omega > 0$

$$\Gamma_{\alpha\beta}^0(\omega) = \pi \theta(\alpha-F) \theta(F-\beta) \delta(\omega - \omega_{\alpha\beta}) \quad (4.9)$$

which restricts the particle-hole states in the sums. If we assume that a single particle-hole channel \bar{n} dominates the absorption, Eq.(4.7) gives

$$\text{Im } \alpha(\omega) = \pi \rho(\omega) |D_{\bar{n}}(\omega)|^2 \quad (4.10)$$

where $\rho(\omega)$ is the density of final states in the particular channel of interest and

$$D_{\bar{n}}(\omega) = \frac{P_{\bar{n}}(\omega)}{1 + i\pi\rho(\omega)\Gamma_{\bar{n}\bar{n}}^0(\omega)} \quad (4.11)$$

Thus

$$\text{Im } \alpha(\omega) = \frac{\pi\rho(\omega)P_{\bar{n}}(\omega)^2}{1 + [\pi\rho(\omega)\Gamma_{\bar{n}\bar{n}}^0(\omega)]^2} \quad (4.12)$$

This is the form first given by Wendin¹⁹⁾. Writing Eq.(4.5) more explicitly we have

$$P_{\alpha\beta} = d_{\alpha\beta} - \sum_{\substack{\lambda > F \\ \mu < F}} \left[\frac{\Gamma_{\alpha\beta;\lambda\mu}^0 P_{\lambda\mu}}{\omega_{\lambda\mu} - \omega} + \frac{\Gamma_{\alpha\beta;\mu\lambda}^0 P_{\mu\lambda}}{\omega_{\lambda\mu} + \omega} \right] \quad (4.13)$$

with a principle part integration being understood. In the RPA, Γ^0 is the direct Coulomb matrix element for which $\Gamma_{\alpha\beta;\lambda\mu}^0 = \Gamma_{\alpha\beta;\mu\lambda}^0$. In this case $P_{\alpha\beta} = P_{\beta\alpha}$ and Eq.(4.13) simplifies to

$$P_{\alpha\beta} = d_{\alpha\beta} - \sum_{\substack{\lambda > F \\ \mu < F}} \Gamma_{\alpha\beta;\lambda\mu}^0 P_{\lambda\mu} \frac{2\omega_{\lambda\mu}}{\omega_{\lambda\mu}^2 - \omega^2} \quad (4.14)$$

If the exchange term is included however, Eq.(4.14) is inappropriate and $P_{\alpha\beta}$ in the RPAE must be calculated using Eq.(4.13). The approximate inclusion of exchange via Eq.(4.14) has sometimes been referred to as the simplified RPAE¹⁶⁾ but it does not have a formal justification.

5. EFFECTIVE POTENTIALS

Eqs.(3.1) and (3.3) can equally well be interpreted in terms of a dynamic self-consistent field. This is most readily seen by transcribing Eq.(3.2) to a co-ordinate representation. We first note that

$$d_{\alpha\beta} = \langle \alpha | z | \beta \rangle \equiv \langle \alpha | \hat{\phi}_{\text{ext}} | \beta \rangle \quad (5.1)$$

where the co-ordinate representation of the externally applied potential is

$$\langle \vec{r} | \hat{\phi}_{\text{ext}} | \vec{r}' \rangle = \phi_{\text{ext}}(\vec{r}) \delta(\vec{r} - \vec{r}') = z \delta(\vec{r} - \vec{r}') \quad (5.2)$$

Likewise we define the effective potential operator according to

$$D_{\alpha\beta}(\omega) \equiv \langle \alpha | \hat{\phi}_{\text{eff}}(\omega) | \beta \rangle \quad (5.3)$$

with the co-ordinate representation

$$\langle \vec{r} | \hat{\phi}_{\text{eff}}(\omega) | \vec{r}' \rangle = \phi_{\text{eff}}(\vec{r}, \vec{r}', \omega) \quad (5.4)$$

Whereas the external potential is local, the complex effective potential in general is not. Finally, we introduce the four-point function

$$\Pi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4, t) = i \langle 0 | T[\psi^\dagger(\vec{r}_2, t) \psi(\vec{r}_1, t) \psi^\dagger(\vec{r}_3) \psi(\vec{r}_4)] | 0 \rangle \quad (5.5)$$

which is related to (2.8) by

$$\Pi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4, t) = \sum_{\lambda\mu} \psi_{\mu}^*(\vec{r}_2) \psi_{\lambda}(\vec{r}_1) \psi_{\alpha}^*(\vec{r}_3) \psi_{\beta}(\vec{r}_4) \Pi_{\lambda\mu; \alpha\beta}(t) \quad (5.6)$$

Similarly,

$$\Pi^0(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4, t) = \sum_{\alpha\beta} \psi_{\beta}^*(\vec{r}_2) \psi_{\alpha}(\vec{r}_1) \psi_{\alpha}^*(\vec{r}_3) \psi_{\beta}(\vec{r}_4) \Pi_{\alpha\beta}^0(t) \quad (5.7)$$

With these definitions, the co-ordinate representation of (3.2) takes the form

$$\begin{aligned} \phi_{\text{eff}}(\vec{r}, \vec{r}', \omega) &= \phi_{\text{ext}}(\vec{r}) \delta(\vec{r}-\vec{r}') \\ &- \delta(\vec{r}-\vec{r}') \iiint d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 v(\vec{r}-\vec{r}_2) \Pi^0(\vec{r}_2, \vec{r}_2, \vec{r}_3, \vec{r}_4, \omega) \phi_{\text{eff}}(\vec{r}_3, \vec{r}_4, \omega) \\ &+ v(\vec{r}-\vec{r}') \iint d\vec{r}_3 d\vec{r}_4 \Pi^0(\vec{r}, \vec{r}', \vec{r}_3, \vec{r}_4, \omega) \phi_{\text{eff}}(\vec{r}_3, \vec{r}_4, \omega) \end{aligned} \quad (5.8)$$

where $v(\vec{r}-\vec{r}')$ is the Coulomb potential. Similarly, Eq.(3.3) becomes

$$\begin{aligned} \alpha(\omega) &= \int d\vec{r} z \int d\vec{r}_1 \int d\vec{r}_2 \Pi^0(\vec{r}, \vec{r}, \vec{r}_1, \vec{r}_2, \omega) \phi_{\text{eff}}(\vec{r}_1, \vec{r}_2, \omega) \\ &\equiv \int d\vec{r} z \delta n(\vec{r}, \omega) \end{aligned} \quad (5.9)$$

which identifies the induced charge density $\delta n(\vec{r}, \omega)$. The second term on the right-hand side of Eq.(5.8) is the electrostatic potential due to the induced charge. The last term is the non-local exchange potential. In the RPA this latter term is neglected and ϕ_{eff} then becomes a local operator satisfying the equation

$$\phi_{\text{eff}}(\vec{r}, \omega) = \phi_{\text{ext}}(\vec{r}) - \int d\vec{r}_1 \int d\vec{r}_2 v(\vec{r}-\vec{r}_1) \Pi^0(\vec{r}_1, \vec{r}_1, \vec{r}_2, \vec{r}_2, \omega) \phi_{\text{eff}}(\vec{r}_2, \omega) \quad (5.10)$$

The quantity $\Pi^0(\vec{r}_1, \vec{r}_1, \vec{r}_2, \vec{r}_2, \omega) \equiv \Pi^0(\vec{r}_1, \vec{r}_2, \omega)$ is just the independent particle density response function. Eq.(5.10) is of the same form as obtained in the time-dependent density functional theory; however in the latter, $v(\vec{r}-\vec{r}')$ is augmented by a local exchange-correlation potential $v_{\text{xc}}'(\vec{r}) \delta(\vec{r}-\vec{r}')$ which constitutes the TDLDA. This term can be viewed as an approximate representation of the HF exchange term in Eq.(5.8) whose inclusion constitutes the full RPAE.

It should be noted that an integral equation for the induced density $\delta n(\vec{r}, \omega)$ is obtained only in the RPA or TDLDA. The RPAE requires a solution for the non-local effective potential in Eq.(5.8) or equivalently, the density matrix $\rho(\vec{r}, \vec{r}', \omega)$ defined by

$$\begin{aligned} \rho(\vec{r}, \vec{r}', \omega) &= \int d\vec{r}_1 \int d\vec{r}_2 \Pi^0(\vec{r}, \vec{r}', \vec{r}_1, \vec{r}_2, \omega) \phi_{\text{eff}}(\vec{r}_1, \vec{r}_2, \omega) \\ &= \int d\vec{r}_1 \Pi^0(\vec{r}, \vec{r}', \vec{r}_1, \vec{r}_1, \omega) \phi_{\text{ext}}(\vec{r}_1) \\ &- \int d\vec{r}_1 \int d\vec{r}_2 \Pi^0(\vec{r}, \vec{r}', \vec{r}_1, \vec{r}_1, \omega) v(\vec{r}_1-\vec{r}_2) \rho(\vec{r}_2, \vec{r}_2, \omega) \\ &+ \int d\vec{r}_1 \int d\vec{r}_2 \Pi^0(\vec{r}, \vec{r}', \vec{r}_1, \vec{r}_2, \omega) v(\vec{r}_1-\vec{r}_2) \rho(\vec{r}_1, \vec{r}_2, \omega) \end{aligned} \quad (5.11)$$

Only the diagonal component of the density matrix is actually required to obtain the polarizability in Eq.(5.9). Previously, the RPAE was solved in terms of the effective dipole matrix element, Eq.(3.2), or an effective particle-hole interaction. A solution in terms of the density matrix requires the four-point function $\Pi^0(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4, \omega)$. Although we shall not carry out this solution here, we display for completeness its functional form

$$\begin{aligned} \Pi^0(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4, \omega) &= \sum_{\alpha < F} \{ \psi_{\alpha}^*(\vec{r}_2) \psi_{\alpha}(\vec{r}_4) G(\vec{r}_1, \vec{r}_3, \omega_{\alpha} + \omega) \\ &+ \psi_{\alpha}(\vec{r}_1) \psi_{\alpha}^*(\vec{r}_3) G(\vec{r}_4, \vec{r}_2, \omega_{\alpha} - \omega) \} \\ &+ \sum_{\substack{\alpha < F \\ \beta < F}} \psi_{\beta}^*(\vec{r}_2) \psi_{\alpha}(\vec{r}_1) \psi_{\alpha}^*(\vec{r}_3) \psi_{\beta}(\vec{r}_4) 2\pi i \delta(\omega - \omega_{\alpha\beta}) \end{aligned} \quad (5.12)$$

where $G(\vec{r}, \vec{r}', \omega)$ is the single-particle Green's function

$$G(\vec{r}, \vec{r}', \omega) = \sum_{\alpha} \frac{\psi_{\alpha}(\vec{r}) \psi_{\alpha}^*(\vec{r}')}{\omega - \omega_{\alpha} + i\delta} \quad (5.13)$$

The terms in Eq.(5.12) involving the delta functions in fact cancel similar singular terms in the bracketed part of Eq.(5.12), as they must since transitions between occupied levels are not allowed. They arise since Π^0 is a time-ordered response function. The referred to cancellation can also be achieved by simply replacing the second Green's function in Eq.(5.13) by its advanced counterpart $G^{\dagger}(\vec{r}_2, \vec{r}_4, \omega_{\alpha} - \omega)$.

6. REACTION MATRIX METHOD

The expression for $\text{Im}\alpha(\omega)$ in Eq.(4.12) may also be obtained by the reaction matrix method^{12), 20)}. We use Eqs.(3.2) and (3.3) for this consideration. For $\omega > 0$, the integral equation for $D_{\alpha}(\omega)$ in Eq.(3.2) is

separated into two real coupled equations for $D_n^i(\omega)$, the real part and $D_n^u(\omega)$ the imaginary part of $D_n(\omega)$ as

$$D_n^i = d_n + \pi \Gamma_{n\omega}^0 D_n^u - \sum_{n'} R_{nn'} D_n^i, \quad (a) \quad (6.1)$$

$$D_n^u = -\pi \Gamma_{n\omega}^0 D_n^i - \sum_{n'} R_{nn'} D_n^u, \quad (b)$$

In the above we have introduced the real matrix $R_{nn'}$, the reaction matrix, by

$$R_{nn'} = \Gamma_{nn'}^0 P\left(\frac{2\omega_{n'}}{\omega_{n'}^2 - \omega^2}\right) = \Gamma_{nn'}^0, R_{n'}^0 \quad (6.2)$$

with

$$\Pi_n^0(\omega) = R_n^0 + i1_n^0 = R_n^0 + i\pi\delta(\omega - \omega_n) \quad (6.3)$$

A bar across a summation sign means a principle part summation or integration over the continuum is implied. We first solve for D_n^u in Eq.(6.1b) to obtain

$$D_n^u = -\pi D_n^i \Gamma_{n\omega}^0(\omega) \quad (6.4)$$

where in general the effective matrix $\Gamma_{nn'}(\omega)$ in Eq.(6.4) is related to the Coulomb interaction matrix $\Gamma_{nn'}^0$ (including exchange) by

$$\Gamma_{nn'}(\omega) = \sum_{n''} (1 + R)_{nn''}^{-1} \Gamma_{n''n'}^0 \quad (6.5)$$

On reinversion the above gives

$$\Gamma_{nn'}(\omega) = \Gamma_{nn'}^0 - \sum_{n''} \Gamma_{nn''}^0 R_{n''n'}^0 \Gamma_{n''n'}(\omega) \quad (6.6)$$

We now solve for D_n^i by substituting for D_n^u from Eq.(6.4) into Eq.(6.1a) to obtain

$$D_n^i = f_n - \pi^2 D_n^i \Gamma_{\omega\omega}^0(\omega) \Gamma_{n\omega}^0(\omega) \quad (6.7)$$

where

$$f_n = \sum_{n'} (1 + R)_{nn'}^{-1} d_{n'} \quad (6.8)$$

By first setting the index $n = \omega$ we find from Eq.(6.7) that

$$D_n^i = f_n / [1 + \{\pi \Gamma_{\omega\omega}^0(\omega)\}^2] \quad (6.9)$$

With the values D_n^i and D_n^u from Eqs.(6.4) and (6.9) we obtain by taking the imaginary part of Eq.(3.3) that

$$\begin{aligned} \text{Im } \alpha(\omega) &= \text{Im} \sum_n d_n \Pi_n^0(\omega) D_n(\omega) \\ &= \pi D_n^i \tilde{P}_\omega^0(\omega) = \pi f_\omega \tilde{P}_\omega^0(\omega) / [1 + \{\pi \Gamma_{\omega\omega}^0(\omega)\}^2] \end{aligned} \quad (6.10)$$

where the function \tilde{P} is in general given by

$$\tilde{P}_n^0(\omega) = d_n - \sum_{n'} R_{n'n}^0 d_{n'} \Gamma_{n'n}(\omega) \quad (6.11)$$

Eq.(6.11) suggests defining the adjoint function \tilde{P}_n^+ by

$$\begin{aligned} \tilde{P}_n^+(\omega) &= d_n - \sum_{n'} \Gamma_{nn'}^0(\omega) R_{n'n}^0 d_{n'} \\ &= d_n - \sum_{n'n''} \Gamma_{nn''}^0 (1 + R)_{n''n'}^{-1} R_{n'n}^0 d_{n'} \end{aligned} \quad (6.12)$$

Finally we see from Eq.(6.10) that knowledge of f_ω is required to determine the expression for $\text{Im} \alpha(\omega)$. Eq.(6.8) on reinversion becomes

$$\begin{aligned} f_n &= d_n - \sum_{n'} R_{nn'} f_{n'} \\ &= d_n - \sum_{n'} R_{nn'} \sum_{n''} (1 + R)_{n''n'}^{-1} d_{n''} \\ &= d_n - \sum_{n'n''} \Gamma_{nn''}^0 (1 + R)_{n''n'}^{-1} R_{n'n}^0 d_{n''} \end{aligned} \quad (6.13)$$

Comparison of Eqs.(6.12) and (6.13) shows that $f_\omega = P_\omega^+(\omega)$, so that

$$\text{Im } \alpha(\omega) = \frac{\pi \tilde{P}_\omega^+(\omega) \tilde{P}_\omega^0(\omega)}{1 + \{\pi \Gamma_{\omega\omega}^0(\omega)\}^2} \quad (6.14)$$

This is the Mukhopadhyay-Lundqvist expression for $\text{Im} \alpha(\omega)$.²⁰⁾ However, since $\Gamma_{nn'}^0$ is symmetric in the indices implies that $P_\omega^+(\omega) = P_\omega^0(\omega)$, thereby arriving

at the expression for $\text{Im}\alpha(\omega)$ first given by Wendin¹⁹⁾. We note finally that $\tilde{P}_n(\omega)$ is just the polarization function defined by Eq.(4.5). This is readily seen by iteration of Eq.(4.5), namely

$$\begin{aligned} P_n(\omega) &= d_n - \sum_{n'} \Gamma_{nn'}^0 R_{n'}^0 d_n' + \sum_{n''} \Gamma_{nn''}^0 R_{n''}^0 \Gamma_{n'n''}^0 d_{n''} + \dots \\ &= d_n - \sum_{n'} \Gamma_{nn'}(\omega) R_{n'}^0 d_{n'} \equiv \tilde{P}_n(\omega) \end{aligned} \quad (6.15)$$

Note in particular that Eq.(6.14) does not embody the density of states factor $\rho(\omega)$. This is because of using the second form of the expression for $D_n(\omega)$ in Eq.(4.8), thus making the contact with the earlier work^{19),20)} more apparent.

In conclusion we have demonstrated the connection between the different formulations for calculating atomic photoabsorption cross sections all of which may be viewed from the self-consistent picture of the electron-electron interactions. The TDLDA method has provided both surprisingly accurate results and great economy in numerical computation. Being a dynamical problem, its major setback is the approximate treatment of the non-local exchange interaction between the electrons via the "adiabatic" LDA. Perhaps a better way of alleviating part of this handicap is to incorporate the recently proposed "dynamic" LDA²¹⁾ at the level of Eq.(5.11) for the calculation of a more meaningful induced density matrix $\rho(\vec{r}, \vec{r}', \omega)$.

ACKNOWLEDGMENTS

One of us (K.N) would like to thank Professor Abdus Salam, the International Atomic Energy Agency and UNESCO for hospitality at the International Centre for Theoretical Physics, Trieste. He would also like to express his gratitude to NSERC of Canada for partly financing a visit to Kingston, Ontario, where this work was initiated.

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FIGURE CAPTIONS

Fig.1 Feynman diagram describing the Coulomb matrix element (a) direct and (b) exchange.

Fig.2 Diagram for the first order contribution to $\alpha(\omega)$.

Fig.3 Diagrammatic representation of Eq.(4.4) in the text.

Fig.4 Diagram representing the lowest order contribution to the imaginary part of $\alpha(\omega)$ ($m = 0$ graph).

Fig.5 Diagram for the renormalized dipole matrix vertices of Fig.4 as explained in the text.

Fig.6 Diagram representing the basic first order contribution to the imaginary part of $\alpha(\omega)$ ($m = 1$ graph).

Fig.7 Diagram for the renormalized dipole matrix and the Coulomb interaction matrix vertices of Fig.6 as described in the text.

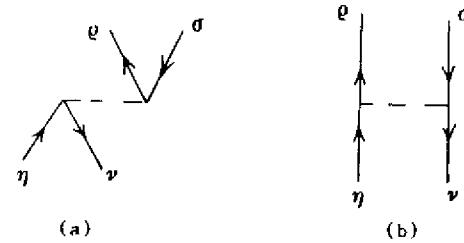


Fig.1

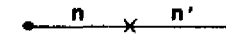


Fig.2

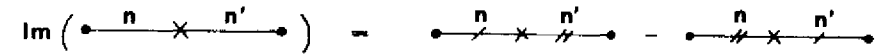


Fig.3



Fig. 4

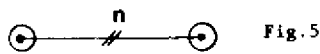


Fig. 5

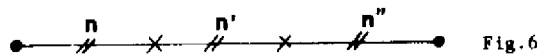


Fig. 6

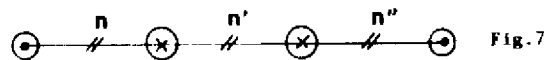


Fig. 7