Many-body theory of effective local potentials for electronic excitations.
II. General theory

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The major purpose of the present paper is to find effective energy-dependent one-electron potentials for core excitations in atoms and solids in terms of the frequency-dependent density response of the system. In the case of the photoionization amplitude we demonstrate how all effects of many-electron interactions within the random phase approximation with exchange (RPAE) can be represented by an effective one-electron wave function or an effective, nonlocal, electron-photon interaction. We also demonstrate the usefulness of intermediate schemes with one-electron basis states of the Hartree-Fock average-of-configuration potentials (V^{N-1}) or the local-density approximation (LDA) with which one calculates the density response within the RPA (no "exchange"), and we make some comparisons with the time-dependent LDA. We also demonstrate how the form of an effective one-electron wave function depends on the choice of dipole-length or dipole-velocity operator. We finally express the RPAE photoionization amplitude in terms of an average amplitude with a Hartree-Fock ^1P wave function and an average dipole-length–dipole-velocity operator and a correction with a correlation wave function and a difference dipole-length–dipole-velocity operator.

I. INTRODUCTION

Many-electron effects play a fundamental role in electronic excitation spectra of atoms, molecules, and solids. Although the bulk of the oscillator strength distribution in most atomic or atomiclike systems is associated with one-electron excitations, many-electron polarization, and relaxation effects often provide essential modifications of the independent-particle picture.

A well-known example of many-electron polarization is the collective dynamics of the $4d$ shell in xenon.[1-14] These collective effects are equally important for the $4d$ shell of the surrounding elements[15-24] and the $5d$ shell of the elements in the region of radon.[12-14,25-29] Moreover, collective effects also determine the behavior of the outer shells of Ar, Kr, Xe, Rn, and the surrounding elements.[3,5,8,12-17,21,26,30-33] In the case of Ba and La, Wendin[15] introduced the concept of *giant dipole resonance*, borrowed from nuclear physics, to describe the collective and resonant behavior of the $4d$ and $5p$ shells. This terminology is now widely used to describe collective inner-shell excitations in atoms, molecules, and solids, in particular, at the beginning of the various d transition-metal series, the $4f$ rare earths and the $5f$ actinides.

The purpose of the present work is to define and to derive one-electron type of local potentials which are able to describe excited states in general, and collective effects and giant dipole resonances in particular. Many-electron effects may be described in terms of response functions representing screening, relaxation, and correlation. In the present work we consider the problem of ionization of an atomic-like system by a frequency-dependent external potential. We use dielectric response theory on the level of the random-phase approximation with exchange[3,12,19,21,30,33] (RPAE) to demonstrate how polarization (screening) effects can be put entirely either into an *effective perturbation* driving the ionization process, or into an *effective one-electron wave function* for the photoelectron.

In particular, we shall demonstrate how polarization and correlation within the RPAE may be represented in terms of an effective one-electron wave function and an associated *energy-dependent effective local potential for excited states*. Characteristic for this effective potential is that the many-electron effects (collective effects, relaxation) mainly influence the *core (inner-well) region*, which determines the overall distribution of oscillator strength of the giant dipole resonance and makes it quite insensitive to the chemical environment.

Whether the oscillator strength distribution is discrete or continuous, or both, depends on the energetic position of the inner-well region relative to the outer part of the potential. This position depends on the character of the transition (s-p, p-d, d-f, etc.) and on the ionization stage. Moreover, it is here that the atomic, molecular, or solid character of the system appears: In a molecule or a solid the resonances in the molecular potential well (shape resonances, near-neighbor multiple scattering) may more or less strongly modulate the inner-well collective resonance. Again, the canonical example is solid Xe,[34] the $4d$-photoabsorption cross section of which shows pronounced oscillations around the atomic one. Very strong modulation of the atomic cross section occurs in the $4d$-photoabsorption spectra of Ba and La halides.[35,36] Very

strong modulation also occurs in photoemission from adsorbates, e.g., Te adsorbed on Ni.[24,37]

In a previous paper,[38] hereafter referred to as paper I, we have given an extensive overview of how polarization and relaxation effects influence the dynamics of electronic excitations in atomic-like systems. In paper I our interest was focused on effective one-electron potentials which can be directly obtained within the HF (Hartree-Fock) or LDA (local-density approximation; see Ref. 8) schemes.

In particular, in an application to atomic Ba, within the HF picture we investigated how the ground-state potential applied to excited states (HF V^N) changed upon inclusion of a spherically averaged core hole (HF$_{av}$ V^{N-1}) and further changed upon inclusion of relaxation and polarization effects (LS dependent HF, HF$_{LS}$ V^{N-1}). Moreover, we compared HF and LDA potentials and found that the ground-state LDA potential was closely similar to the relaxed ($4\underline{d}\epsilon f$) HF$_{av}$ V^{N-1} potential in the core region. We concluded that the LDA potential effectively contains a hole in the core region and we gave a motivation for our view that the LDA self-interaction simulates relaxation.

The plan of the present paper is the following. In Sec. II we discuss one-electron potentials and independent-electron pictures. In Sec. III we develop a scheme which describes the photoionization matrix element in terms of many-electron response functions (dielectric functions), and give our definitions of *effective electron-photon interaction* and *effective one-electron wave function*.

In Sec. IV all effects of electron-electron interaction within the RPAE are taken into account by an effective one-electron wave function. We can then represent the RPAE transition amplitude in terms of an effective energy-dependent wave function and potential for the photoelectron, and explicitly study the effect of ground-state (initial-state) correlations in the discrete region and in the continuum (the first results of this kind appeared in Refs. 39 and 40). The price we have to pay is that the RPAE wave function becomes *operator dependent*: It will depend on whether we use the dipole-length (**E·r**) or dipole-velocity (**A·p**) form of the electron-photon interaction when calculating photoionization matrix elements.

In Sec. V we consider the case that all effects of electron-electron interaction (RPAE bubble *and* ladder interaction) are incorporated into a *nonlocal effective electron-photon interaction*. This nonlocality is solely due to the ladder interaction. We then devise a scheme for constructing a local, energy-dependent ladder interaction, closely related to the Talman-Shadwick scheme[38] for a local exchange interaction.

Section VI discusses how to reduce or remove the nonlocality by choosing the independent-electron picture to incorporate most of the electron-hole ladder interaction. We also describe the local-density random-phase approximation (LDRPA) scheme[13,26] (RPA bubble interaction and LDA basis) and discuss possible connections with the TDLDA (time-dependent LDA).[8,23]

In Sec. VII, finally, we analyze the properties of the dipole-length and dipole-velocity forms of the RPAE transition matrix elements. The RPAE effective wave functions is written in terms of a final-state contribution (TDAE, Tamm-Dancoff approximation with exchange)

and an initial-state contribution (correlation). As a result, the RPAE ionization amplitude may be expressed as the sum of a TDAE ($=$HP ^1P) amplitude with an *average* length-velocity operator, and a *correlation* amplitude with a *difference* length-velocity operator.

II. ONE-ELECTRON POTENTIALS IN THE INDEPENDENT-ELECTRON PICTURE

The many-electron response formalism to be employed in subsequent sections is developed using a basis of one-electron states. We refer to paper I (Ref. 38) for an extensive discussion of one-electron wave functions and for references to other work. Below we only give a summary of necessary concepts and definitions.

In the one-electron approximation, the central electrostatic potential defines a basis of independent-electron wave functions $\phi_i(\mathbf{r})$ via the Schrödinger equation (Ry units)

$$[-\nabla^2 + V_i(\mathbf{r})]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) . \qquad (2.1)$$

In the general case, the potential $V_i(\mathbf{r})$ is nonlocal and state dependent and may be written as

$$V_i(\mathbf{r}) = -2z/r + V_H(\mathbf{r}) + V_{i\,\mathrm{xc}}(\mathbf{r}) , \qquad (2.2)$$

where $V_H(\mathbf{r})$ is the Hartree potential and $V_{i\,\mathrm{xc}}(\mathbf{r})$ is a state-dependent exchange-correlation potential. Denoting the Coulomb interaction by (Ry units)

$$V(\mathbf{r},\mathbf{r}') = 2\,|\,\mathbf{r} - \mathbf{r}'\,|^{-1} \qquad (2.3)$$

the Hartree potential is given by

$$V_H(\mathbf{r}) = \sum_k \int d\mathbf{r}'\, V(\mathbf{r},\mathbf{r}')\,|\,\phi_k(\mathbf{r}')\,|^2 . \qquad (2.4)$$

We shall mainly be concerned with Hartree-Fock one-electron states; the exchange-correlation potential is then given by the pure exchange potential

$$\begin{aligned} V_{i\,\mathrm{xc}}(\mathbf{r}) &= V_{ix}(\mathbf{r}) \\ &= \phi_i(\mathbf{r})^{-1}\int V_x(\mathbf{r},\mathbf{r}')\phi_i(\mathbf{r}')d\mathbf{r}' \\ &= \phi_i(\mathbf{r})^{-1}X_i(\mathbf{r}) , \end{aligned} \qquad (2.5)$$

where

$$V_x(\mathbf{r},\mathbf{r}') = -V(\mathbf{r},\mathbf{r}')n(\mathbf{r},\mathbf{r}') , \qquad (2.6a)$$

$$n(\mathbf{r},\mathbf{r}') = \sum_k \phi_k(\mathbf{r})\phi_k^*(\mathbf{r}') , \qquad (2.6b)$$

$V_x(\mathbf{r},\mathbf{r}')$ is the usual nonlocal orbital independent exchange potential, and $n(\mathbf{r},\mathbf{r}')$ is the one-particle density matrix. The summations in Eqs. (2.4) and (2.6) run over all N electrons, and therefore contain Hartree and exchange self-interactions.

Since the one-electron potential is spherically symmetric we may separate out all angular dependence and work with radial wave functions $u_n(r)$ defined by

$$\phi_n(\mathbf{r}) = r^{-1}u_n(r)Y_{lm}(\theta,\phi) \qquad (2.7)$$

and given by the radial Schrödinger equation

$$[-d^2/dr^2 + V_n^{\mathrm{eff}}(r)]u_n(r) = \epsilon_n u_n(r) , \qquad (2.8)$$

where

$$V_n^{\text{eff}}(r) = V_n(r) + l(l+1)/r^2 \tag{2.9}$$

is the effective radial potential including the centrifugal term. The one-electron potential $V_n(r)$ can be written as [Eqs. (2.3)–(2.6)]

$$V_n(r) = -2Z/r + V_H(r) + X_n(r)/u_n(r) , \tag{2.10}$$

where the Hartree and exchange potentials $V_H(r)$ and $X_n(r)/u_n(r)$ can be expressed in terms of multipole contributions.[41]

In the *ground state,* the Coulomb and exchange self-interactions cancel; the resulting potential has a Coulomb tail and represents interaction with $N-1$ electrons, a so called HF V^{N-1} potential. However, when constructing *potentials for excited states* using the *ground-state orbitals,* there is no longer automatic cancellation of self-interactions: If the ground-state HF operator is employed, the resulting potential has no Coulomb tail. This so called HF V^N neutral-atom potential describes the potential for *adding* an electron to the frozen N-electron system.

For some of the later applications it is essential that the HF one-electron potential $V_n(r)$ in Eq. (2.10) is the same, or at least very similar, for ground and excited states. This may be accomplished by explicitly removing the Coulomb and exchange self-interactions in the HF V^N potential. We thus define a self-interaction-free so-called frozen-core HF$_\text{av}$ V^{N-1} ionic potential, corresponding to a spherically averaged hole in a specific one-electron orbital i of the ground-state charge distribution.

The frozen-core HF$_\text{av}$ V^{N-1} ionic potential for an excited electron is very close to the potential seen by the same electron in the ground state. It represents one-electron excitation in the absence of any kind of response, like polarization or relaxation, and will therefore be employed as a zeroth-order basis set for describing the many-electron response.

We finally note that by not performing any spherical average over the hole $\underline{i}$, one may construct an *LS-dependent* HF V^{N-1} ionic potential for excited states, based on a frozen or relaxed core.[38,42] Such a potential incorporates many-electron effects in the final-state but omits initial-state effects.

If the wave function is known in numerical form, the radial Schrödinger equation (2.8) may be inverted to give the effective local potential

$$V_n^{\text{eff}}(r) = u_n(r)^{-1}(d^2/dr^2 + \epsilon_n)u_n(r) . \tag{2.11}$$

This relation is essential in all those cases where we use many-body theory (e.g., the RPAE) to arrive directly at an approximate effective one-electron wave function, and subsequently want to find an associated local potential.

III. LINEAR RESPONSE THEORY OF THE EFFECTIVE IONIZATION AMPLITUDE

In this section we shall focus attention on dynamic polarization (induced field) effects, which modify the independent-electron ionization amplitude.

We shall not consider many-electron descriptions of relaxation and shake-up. The core hole and the photoelec-

tron will be treated in independent-electron approximations. The spectrum of emitted electrons thus consists of single photoelectron (PE) peaks, one for each subshell, without any satellite structure.

Let us consider ionization by an external potential with frequency $\omega, v_{\text{ext}}(\mathbf{r};\omega)$, not necessarily any dipole potential. The resulting one-electron ionization amplitude has the form

$$M_{\epsilon i} = \langle \epsilon | v_{\text{ext}}(\mathbf{r};\omega) | i \rangle \tag{3.1a}$$

$$= \int d\mathbf{r}\, \phi_\epsilon^*(\mathbf{r}) v_{\text{ext}}(\mathbf{r};\omega) \phi_i(\mathbf{r}) , \tag{3.1b}$$

which goes over into an effective ionization amplitude $M_{\epsilon i}(\omega)$,

$$M_{\epsilon i} \rightarrow M_{\epsilon i}(\omega) \tag{3.2}$$

under the influence of polarization effects.

The effective ionization amplitude $M_{\epsilon i}(\omega)$ can be calculated directly within a matrix formulation using finite- or infinite-order perturbation theory.[3–6,13,15–22] In this work we prefer to use space representations in terms of effective perturbations and effective wave functions

$$M_{\epsilon i}(\omega) = \langle \epsilon_{\text{eff}} | v_{\text{eff}}(\mathbf{r},\mathbf{r}';\omega) | i \rangle \tag{3.3a}$$

$$= \int d\mathbf{r}\, d\mathbf{r}'\, \phi_\epsilon^{\text{eff}*}(\mathbf{r}) v_{\text{eff}}(\mathbf{r},\mathbf{r}';\omega) \phi_i(\mathbf{r}') . \tag{3.3b}$$

Many-electron effects can be put into either the effective nonlocal perturbation $v_{\text{eff}}(\mathbf{r},\mathbf{r}';\omega)$ or the effective wave function $\phi_\epsilon^{\text{eff}*}(\mathbf{r})$ or into both of them, as indicated in Eq. (3.3). A question of some interest concerns whether certain effects are more naturally referred to v_{eff} than to $\phi_\epsilon^{\text{eff}}$, or vice versa. Strictly speaking, this is a semantic question: The only unique physical quantity is the ionization amplitude $M_{\epsilon i}(\omega)$, and the division into v^{eff} and ϕ^{eff} rather reflects on different physical pictures, different computational techniques, and different fields of physics. For instance, in condensed matter physics it is natural to consider electrons to be emitted by the action of screened, effective perturbations, while in atomic physics one often works with effective (e.g., LS coupled) one-electron wave functions and bare external or internal interactions.

In a mixed, condensed-matter inspired, approach such as Eq. (3.3) the screening of the external perturbation may go into $v_{\text{eff}}(\mathbf{r},\mathbf{r}';\omega)$, while the effect of the core-hole potential may be taken into account by the photoelectron wave function $\phi_\epsilon^{\text{eff}}(\mathbf{r})$. Core-hole induced relaxation will, in particular, screen the spherical part of the core-hole potential and may be approximately taken into account by calculating the effective one-electron wave function $\phi_\epsilon^{\text{eff}}(\mathbf{r})$ in the potential of the relaxed ion. However, since the dynamic response is evaluated using $\phi_\epsilon^{\text{eff}}(r)$, relaxation will also be incorporated into the effective perturbation $v_{\text{eff}}(\mathbf{r},\mathbf{r}';\omega)$ which drives the ionization process.

In order to demonstrate the equivalence of different representations of the effective ionization amplitude $M_{\epsilon i}(\omega)$, we shall rewrite Eq. (3.3) to describe two extreme cases,

$$M_{\epsilon i}(\omega) \rightarrow \begin{cases} \langle \epsilon_{\text{eff}} | v_{\text{ext}}(\mathbf{r};\omega) | i \rangle & (3.4a) \\ \langle \epsilon | v_{\text{eff}}(\mathbf{r},\mathbf{r}';\omega) | i \rangle , & (3.4b) \end{cases}$$
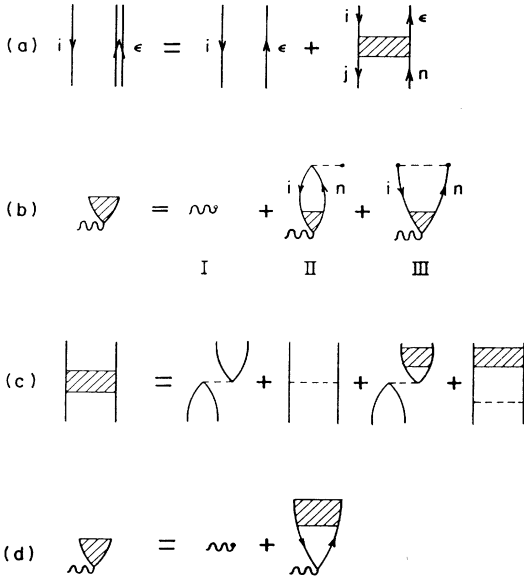
FIG. 1. Diagrammatic representations of effective wave functions and interactions within the random-phase approximation with exchange (RPAE): (a) effective wave function $\phi_\epsilon^{\text{eff}}(\mathbf{r})$; (b) and (d) effective electron-photon interaction $v_{\text{eff}}(\mathbf{r},\mathbf{r}';\omega)$; (c) effective electron-hole interaction Γ.

where all many-electron effects within the RPAE have been put into either ϕ^{eff} [Eq. (3.4a); Fig. 1(a)] or v_{eff} [Eq. (3.4b); Fig. 1(b)]. All the formulations in Eqs. (3.3) and (3.4) can be related via a frequency-dependent nonlocal function $X=X(\mathbf{r}_3\mathbf{r}_4;\mathbf{r}_1\mathbf{r}_2;\omega)$, which describes the linear response of the system to a weak external perturbation v_{ext}. Below we present a condensed description of some important relations from standard linear response theory,[43,44] which we need for describing v_{eff} and $\phi_\epsilon^{\text{eff}}$.

We shall use operator notation for X, v_{ext}, v_{eff}, etc. to describe the general relations governing the response, and explicit space representations will only be introduced when necessary.

Application of the external potential v_{ext} leads to polarization and gives rise to an induced density δn, an induced potential $v_{\text{ind}}=V\delta n$, and to an effective potential v_{eff} [Fig. 1(b)]

$$v_{\text{eff}}=v_{\text{ext}}+v_{\text{ind}} , \tag{3.5}$$

$$v_{\text{ind}}=V\delta n \tag{3.6a}$$

$$=VX v_{\text{ext}} . \tag{3.6b}$$

The induced potential may be represented in terms of the response function X_0 for the system of noninteracting electron-hole pairs and the effective electron-hole interaction Γ [Fig. 1(c)] according to

$$VX=\Gamma X_0 , \tag{3.7}$$

$$X v_{\text{ext}}=X_0 v_{\text{eff}} . \tag{3.8}$$

In this manner, Eq. (3.5) may be written in a number of useful ways,

$$v_{\text{eff}}=v_{\text{ext}}+VX v_{\text{ext}} \tag{3.9}$$

$$=v_{\text{ext}}+\Gamma X_0 v_{\text{ext}} \tag{3.10}$$

$$=v_{\text{ext}}+VX_0 v_{\text{eff}} . \tag{3.11}$$

Equations (3.10) and (3.11) refer to Figs. 1(d) and 1(b), respectively.

These equations are equivalent to the well-known integral equations for the dielectric susceptibility (response function) X

$$X=X_0+XVX_0 \tag{3.12}$$

or the effective electron-hole interaction Γ [corresponding to Fig. 1(c)]

$$\Gamma=V+\Gamma X_0 V \tag{3.13}$$

(Bethe-Salpeter equation). From Eq. (3.10) we may define an inverse dielectric function

$$v_{\text{eff}}=\epsilon^{-1}v_{\text{ext}} , \tag{3.14}$$

$$\epsilon^{-1}=1+\Gamma X_0 . \tag{3.15}$$

With the use of Eqs. (3.4b) and (3.14), the effective ionization amplitude $M_{\epsilon i}(\omega)$ may be written as

$$M_{\epsilon i}(\omega)$$

$$=\langle \epsilon | \int d\mathbf{r}_1 \epsilon^{-1}(\mathbf{r}\mathbf{r}';\mathbf{r}_1\mathbf{r}_1;\omega)v_{\text{ext}}(\mathbf{r}_1;\omega) | i \rangle \tag{3.16a}$$

$$=\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}_1\phi_\epsilon^*(\mathbf{r})\phi_i(\mathbf{r}')\epsilon^{-1}(\mathbf{r}\mathbf{r}';\mathbf{r}_1\mathbf{r}_1;\omega)$$

$$\times v_{\text{ext}}(\mathbf{r}_1;\omega) . \tag{3.16b}$$

The effective wave function form of $M_{\epsilon i}(\omega)$ in Eq. (3.4a) can now easily be obtained from Eq. (3.16b),

$$M_{\epsilon i}(\omega)=\langle \epsilon_{\text{eff}} | v_{\text{ext}}(\mathbf{r}_1;\omega) | i \rangle \tag{3.17a}$$

$$=\int d\mathbf{r}_1\phi_\epsilon^{\text{eff}*}(\mathbf{r}_1;\omega)\phi_i(\mathbf{r}_1)v_{\text{ext}}(\mathbf{r}_1;\omega) , \tag{3.17b}$$

where

$$\phi_\epsilon^{\text{eff}*}(\mathbf{r}_1;\omega)\phi_i(\mathbf{r}_1)=\int d\mathbf{r}\,d\mathbf{r}'\,\phi_\epsilon^*(\mathbf{r})\phi_i(\mathbf{r}')\epsilon^{-1}(\mathbf{r}\mathbf{r}';\mathbf{r}_1\mathbf{r}_1;\omega) .$$

$$\tag{3.18}$$

Through the wave function formulation in Eqs. (3.17) and (3.18) we now have a link between the dielectric response function and the effective-field approach on the one hand, and direct methods for calculating wave functions on the other.

IV. EFFECTIVE WAVE-FUNCTION FORMULATION

In this section we shall discuss methods in which all of the many-electron effects are included in an effective wave function which gives an effective photoionization amplitude

$$M_{\epsilon i}(\omega)=\langle \epsilon_{\text{eff}} | v_{\text{ext}}(\mathbf{r};\omega) | i \rangle . \tag{4.1}$$

The necessary formalism has been developed in Sec. III. Inserting the space representation of Eq. (3.15) into Eq. (3.18), we obtain [Fig. 1(a)]

$$\phi_\epsilon^{\text{eff}*}(\mathbf{r};\omega)\phi_i(\mathbf{r}) = \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_\epsilon^*(\mathbf{r}_1)\phi_i(\mathbf{r}_2) \left[\delta(\mathbf{r}-\mathbf{r}_1)\delta(\mathbf{r}-\mathbf{r}_2) + \int d\mathbf{r}_3 d\mathbf{r}_4 \Gamma(\mathbf{r}_1\mathbf{r}_2;\mathbf{r}_3\mathbf{r}_4;\omega)\chi_0(\mathbf{r}_3\mathbf{r}_4;\mathbf{r}\mathbf{r};\omega) \right] . \tag{4.2}$$

Since we have a complete basis of one-electron wave functions, we may write down the spectral resolution of the response function for independent excitations

$$\chi_0(\mathbf{r}_3\mathbf{r}_4;\mathbf{r}_1\mathbf{r}_2;\omega) = -\sum_{n,j} \frac{\phi_n(\mathbf{r}_3)\phi_j^*(\mathbf{r}_4)\phi_n^*(\mathbf{r}_1)\phi_j(\mathbf{r}_2)}{\omega_{nj}-\omega-i\delta\,\text{sgn}(\omega_{nj})}(f_j - f_n) . \tag{4.3}$$

The electron-hole pair excitation energy is defined as $\omega_{nj} = \epsilon_n - \epsilon_j$ and $\sum$ denotes summation over discrete levels and integration over the continuum. f_i and f_n are Fermi factors ($f_k = 1$ if k is occupied, and $f_k = 0$ if k is empty). Using this spectral resolution we obtain [Fig. 1(a)]

$$\phi_\epsilon^{\text{eff}*}(\mathbf{r};\omega) = \phi_\epsilon^*(\mathbf{r})$$
$$+ \sum_{n,j} \frac{\Gamma_{\epsilon jni}(\omega)\phi_n^*(\mathbf{r})}{\omega_{nj}-\omega-i\delta\,\text{sgn}(\omega_{nj})} \frac{\phi_j(\mathbf{r})}{\phi_i(\mathbf{r})}(f_j - f_n) , \tag{4.4}$$

where

$$\Gamma_{\epsilon inj}(\omega) = \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \phi_\epsilon^*(\mathbf{r}_3)\phi_i(\mathbf{r}_4)$$
$$\times \Gamma(\mathbf{r}_3\mathbf{r}_4;\mathbf{r}_1\mathbf{r}_2;\omega)\phi_n(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2) . \tag{4.5}$$

The effective wave function in Eq. (4.3) may also be written in the form

$$\phi_\epsilon^{\text{eff}*}(\mathbf{r};\omega) = \phi_\epsilon^*(\mathbf{r}) + \sum_{\substack{n>F \\ j<F}} \left[\frac{\Gamma_{\epsilon jni}(\omega)\phi_n^*(\mathbf{r})}{\omega_{nj}-\omega-i\delta} \frac{\phi_j(\mathbf{r})}{\phi_i(\mathbf{r})} \right.$$
$$\left. + \frac{\Gamma_{\epsilon nji}(\omega)\phi_n(\mathbf{r})}{\omega_{nj}+\omega} \frac{\phi_j^*(\mathbf{r})}{\phi_i(\mathbf{r})} \right] . \tag{4.6}$$

Here F denotes the Fermi level separating the filled and the empty levels. $\Gamma_{\epsilon jni}(\omega)$ is an effective Coulomb interaction matrix element of the solution of the Bethe-Salpeter equation (3.13) [Fig. 1(c)], and has the form of the random-phase approximation with exchange (RPAE).

Equation (4.6) and Fig. 1(a) show how the zeroth-order excitation $\phi_\epsilon^*(\mathbf{r})\phi_i(\mathbf{r})$ becomes dressed up to an effective excitation, the division by $\phi_i(\mathbf{r})$ leading to an *effective one-electron wave function for the excited state*.

In the following we shall concentrate on excitations within a single channel i-n, e.g., $4d$-ϵf

$$\phi_\epsilon^{\text{eff}*}(\mathbf{r};\omega) = \phi_\epsilon^*(\mathbf{r}) + \sum_{\substack{n>F \\ i'<F}} \left[\frac{\Gamma_{\epsilon i'ni}(\omega)\phi_n^*(\mathbf{r})}{\omega_{ni}-\epsilon-i\delta} \frac{\phi_{i'}(\mathbf{r})}{\phi_i(\mathbf{r})} \right.$$
$$\left. + \frac{\Gamma_{\epsilon ni'i}(\omega)\phi_n(\mathbf{r})}{\omega_{ni}+\omega} \frac{\phi_{i'}^*(\mathbf{r})}{\phi_i(\mathbf{r})} \right] . \tag{4.7}$$

i' distinguishes different (degenerate, $\omega_{ni} = \omega_{ni'}$) magnetic sublevels. The dynamics is contained in the radial

effective wave function, which can be written as

$$u_\epsilon^{\text{eff}*}(r;\omega) = u_\epsilon^{\text{eff}*}(r)$$
$$= u_\epsilon(r) - \sum_n \left[\frac{F_{\epsilon n}(\omega)}{\omega_n - \omega - i\delta} + \frac{K_{\epsilon n}(\omega)}{\omega_n + \omega} \right] u_n(r) , \tag{4.8}$$

where $u_n(r)$ is defined according to Eq. (2.7) and

$$\Gamma_{\epsilon ini}(\omega) \rightarrow -F_{\epsilon n}(\omega) , \tag{4.9a}$$

$$\Gamma_{\epsilon nii}(\omega) \rightarrow -K_{\epsilon n}(\omega) . \tag{4.9b}$$

The angular coefficients have been absorbed into $F_{\epsilon n}(\omega)$ and $K_{\epsilon n}(\omega)$, and $\omega_n = \omega_{ni}$. The change of sign arises because we now take the *bubble* interaction as our reference, instead of the ladder interaction [see, e.g., Fig. 1(b)—1(d)].

As it stands, the radial effective wave function in Eq. (4.8) is *complex*. However, at the same time we know that the radial wave function can be represented as a properly normalized real function. This way it comes out from, e.g., an *LS*-dependent HF calculation [corresponding to the omission of the negative-frequency term in Eq. (4.8)].[19,38,45,46] The connection is known from scattering theory, and we expand the treatment of the RPAE in the Appendix. The result is ($\epsilon = \omega + \epsilon_i$; P $\sum$ denotes principle part integration)

$$u_\epsilon^{\text{eff}*}(r) = [N^*(\omega)]^{-1}$$
$$\times \left[u_\epsilon(r) - P\sum_n [I_{\epsilon n}^>(\omega) + I_{\epsilon n}^<(\omega)]u_n(r) \right] \tag{4.10a}$$

$$= P_\epsilon^{\text{eff}}(r)/N^*(\omega) \tag{4.10b}$$

where $I_{\epsilon n}^>(\omega)$ and $I_{\epsilon n}^<(\omega)$ are positive and negative frequency response functions

$$I_{\epsilon n}^>(\omega) = \frac{V_{\epsilon n}(\omega)}{\omega_n - \omega} , \tag{4.11}$$

$$I_{\epsilon n}^<(\omega) = \frac{G_{\epsilon n}(\omega)}{\omega_n + \omega} , \tag{4.12}$$

$N^*(\omega)$ is a normalization function

$$N^*(\omega) = 1 + i\pi V_{\epsilon\epsilon}(\omega) \tag{4.13}$$

and

$$F_{\epsilon n}(\omega) = [N^*(\omega)]^{-1}V_{\epsilon n}(\omega) , \tag{4.14a}$$

$$I_{\epsilon n}(\omega) = [N^*(\omega)]^{-1}G_{\epsilon n}(\omega) , \tag{4.14b}$$

$V_{\epsilon n}(\omega)$ and $G_{\epsilon n}(\omega)$ are real quantities, given by the reaction matrix equations

$$V_{\epsilon n}(\omega) = V_{\epsilon n} - P\sum_m [I_{\epsilon m}^>(\omega)V_{mn} + I_{\epsilon n}^<(\omega)G_{mn}] , \tag{4.15a}$$

$$G_{\epsilon n}(\omega) = G_{\epsilon n} - P\sum_m [I_{\epsilon m}^>(\omega)G_{mn} + I_{\epsilon n}^<(\omega)V_{mn}] . \tag{4.15b}$$

$V_{\epsilon n}$ and $G_{\epsilon n}$ are zeroth-order matrix elements of the Coulomb interaction appearing in Figs. 1 and 2, representing final- and initial-state interaction, respectively. Assuming that the angular dependence of the external perturbation $v_{ext}(\mathbf{r};\omega)$ is given by the Legendre polynomial $P_L(\cos\theta)$, $V_{\epsilon n}$ and $G_{\epsilon n}$ may be expressed in terms of Slater integrals and $3j$ and $6j$ symbols according to

$$V_{\epsilon n}=a_L R^{L}(\epsilon i;in)-\sum_K b_K R^{K}(\epsilon i;ni) , \qquad (4.16a)$$

$$G_{\epsilon n}=a_L R^{L}(\epsilon n;ii)-\sum_K c_K R^{K}(\epsilon n;ii) , \qquad (4.16b)$$

where $l_\epsilon=l_n$ (single channel), and

$$R^{K}(ab;cd)=\int u_a(r_1)u_b(r_2)\frac{r_<^{K}}{r_>^{K+1}}u_c(r_1)u_d(r_2)dr_1dr_2 , \qquad (4.17)$$

$$a_L=2(2L+1)^{-1}(2l_i+1)(2l_n+1)\begin{vmatrix}l_i & L & l_n\\0 & 0 & 0\end{vmatrix}^2 , \qquad (4.18a)$$

$$b_K=(-1)^{L+1}(2l_i+1)(2l_n+1)$$
$$\times\begin{vmatrix}l_i & K & l_i\\0 & 0 & 0\end{vmatrix}\begin{vmatrix}l_n & K & l_n\\0 & 0 & 0\end{vmatrix}\begin{Bmatrix}l_i & L & l_n\\l_n & K & l_i\end{Bmatrix} , \qquad (4.18b)$$

$$c_K=(-1)^{L+1}(2l_i+1)(2l_n+1)$$
$$\times\begin{vmatrix}l_i & K & l_n\\0 & 0 & 0\end{vmatrix}^2\begin{Bmatrix}l_n & L & l_i\\l_n & K & l_i\end{Bmatrix} . \qquad (4.18c)$$

A normalized real wave function which gives the same ionization probability is then given by

$$u_\epsilon^{eff}(r)=|N(\omega)|^{-1}P_\epsilon^{eff}(r) , \qquad (4.19a)$$

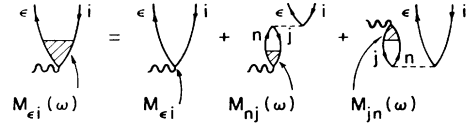$$|N(\omega)|\equiv N=[1+\pi^2 V_{\epsilon\epsilon}(\omega)^2]^{1/2} , \qquad (4.19b)$$

FIG. 2. RPA integral equation for the photoionization amplitude. With inclusion of exchange matrix elements (ladders) one obtains the RPAE.

which makes $u_\epsilon^{eff}(r)$ normalized according to

$$\int u_\epsilon^{eff}(r)u_{\epsilon'}^{eff}(r)dr=\delta(\epsilon'-\epsilon) . \qquad (4.20)$$

In Sec. VII we shall make explicit use of the effective one-electron wave function in Eq. (4.19) in order to study the behavior of the length and velocity forms of the dipole matrix elements. Moreover, in a subsequent paper (III) we shall present extensive numerical results for effective potentials derived from effective wave functions constructed via Eq. (4.19). In paper I we have already presented some such potentials.

V. EFFECTIVE-INTERACTION FORMULATION

A. Nonlocal interaction

In this section we would like to demonstrate how transfer of all effects of electron-hole interaction to the dressing up of v_{ext} leads to a *nonlocal interaction* v_{eff} between the *effective* field and the electrons.

The starting point is the integral equation (3.11) for v_{eff}. In the space representation we explicitly obtain

$$v_{eff}(\mathbf{r},\mathbf{r}';\omega)=v_{ext}(\mathbf{r};\omega)\delta(\mathbf{r}-\mathbf{r}') \qquad (5.1a)$$

$$+\int d\mathbf{r}_1 d\mathbf{r}_2\left[\int d\mathbf{r}'' V(\mathbf{r},\mathbf{r}'')X_0(\mathbf{r}''\mathbf{r}'';\mathbf{r}_1\mathbf{r}_2;\omega)\right]v_{eff}(\mathbf{r}_1,\mathbf{r}_2;\omega) \qquad (5.1b)$$

$$-\int d\mathbf{r}_1 d\mathbf{r}_2[V(\mathbf{r},\mathbf{r}')X_0(\mathbf{r}\mathbf{r}';\mathbf{r}_1\mathbf{r}_2;\omega)]v_{eff}(\mathbf{r}_1,\mathbf{r}_2;\omega) , \qquad (5.1c)$$

(5.1a), (5.1b), and (5.1c) correspond to Figs. 1(bI), 1(bII), and 1(bIII), respectively. Clearly it is the ladder part [Fig. 1(bIII)] that causes "complications:" In the absence of the ladder term (5.1c), v_{eff} would be *local*.

Introducing the spectral resolution (4.3) into Eq. (5.1) we obtain the final and explicit result for the integral equation for the nonlocal, effective perturbation [Fig. 1(b)]

$$v_{eff}(\mathbf{r},\mathbf{r}';\omega)$$

$$=v_{ext}(\mathbf{r};\omega)\delta(\mathbf{r}-\mathbf{r}')$$

$$-\sum_{j,n}\mathscr{Y}_{jn}(\mathbf{r},\mathbf{r}')\frac{f_j-f_n}{\omega_{nj}-\omega-i\delta\,\mathrm{sgn}(\omega_{nj})} \qquad (5.2a)$$

$$\times\langle n\,|\,v_{eff}(\mathbf{r}_1,\mathbf{r}_2;\omega)\,|\,j\rangle , \qquad (5.2b)$$

where

$$\mathscr{Y}_{jn}(\mathbf{r},\mathbf{r}')=Y_{jn}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')-Y_{jn}(\mathbf{r},\mathbf{r}') , \qquad (5.3)$$

$$Y_{jn}(\mathbf{r})=\int d\mathbf{r}'' V(\mathbf{r},\mathbf{r}'')\phi_j^*(\mathbf{r}'')\phi_n(\mathbf{r}'') , \qquad (5.4)$$

$$Y_{jn}(\mathbf{r},\mathbf{r}')=V(\mathbf{r},\mathbf{r}')\phi_j^*(\mathbf{r}')\phi_n(\mathbf{r}) , \qquad (5.5)$$

$Y_{jn}(\mathbf{r})$ is the electrostatic potential from the charge-density displacement associated with the electron-hole pair excitation nj (bubble interaction) and gives rise to a *local induced* potential. $Y_{jn}(\mathbf{r},\mathbf{r}')$ is a pair potential accounting for the direct electrostatic interaction between the electron (n) and the hole (j). This interaction will be screened if core relaxation is taken into account. Moreover, this part of the induced potential is *nonlocal* and is responsible for the nonlocal form of the effective driving potential $v_{eff}(\mathbf{r},\mathbf{r}';\omega)$.

Usually Eq. (5.2) is expressed on matrix form when it comes to practical calculations. For example, inserting (5.2) into Eq. (3.4b) one obtains the well-known RPAE integral equation (Fig. 2)

$$M_{\epsilon i}(\omega) = M_{\epsilon i} - \sum_{j,n} \frac{V_{\epsilon j[in]} M_{nj}(\omega)}{\omega_{nj} - \omega - i\delta \operatorname{sgn}(\omega_{nj})} (f_j - f_n) \qquad (5.6)$$

where, in analogy with Eq. (3.4b),

$$M_{nj}(\omega) = \langle n \mid v_{\text{eff}}(\mathbf{r}_1, \mathbf{r}_2; \omega) \mid j \rangle \qquad (5.7)$$

and

$$V_{\epsilon j[in]} = \langle \epsilon \mid \mathscr{Y}_{jn}(\mathbf{r}, \mathbf{r}') \mid i \rangle \qquad (5.8a)$$

$$= \langle \epsilon j \mid V(\mathbf{r}, \mathbf{r}') \mid in \rangle - \langle \epsilon j \mid V(\mathbf{r}, \mathbf{r}') \mid ni \rangle . \qquad (5.8b)$$

B. Local interaction

The nonlocal effective interaction $v_{\text{eff}}(\mathbf{r}, \mathbf{r}'; \omega)$ in Eq. (5.2) is not a very convenient object to handle numerically. A more convenient scheme would be to define the electron-field interaction to be *local*, $v_{\text{eff}}(\mathbf{r}; \omega)$. This can approximately be done in two ways: Either by (i) removing the ladder interaction from Eq. (5.1) via a suitable *choice of one-electron basis*, as will be discussed in Sec. VI, or by (ii) replacing the ladder interaction by an *equivalent local interaction*.

In paper I we discussed various ways of producing a *local exchange potential* for the ground state. In particular we discussed the Talman-Shadwick (TS) scheme:[47] This scheme may be formulated[38] in terms of the static susceptibility by requiring that the local TS exchange interaction give the same induced density as the nonlocal exchange interaction [Fig. 3(a)]

$$\int d\mathbf{r}_1 \chi_0(\mathbf{r}; \mathbf{r}_1; 0) V_x^{\text{TS}}(\mathbf{r}_1) = \int d\mathbf{r}_1 d\mathbf{r}_2 \chi_0(\mathbf{r}\mathbf{r}; \mathbf{r}_1\mathbf{r}_2; 0) V_x(\mathbf{r}_1, \mathbf{r}_2) , \qquad (5.9)$$

or, introducing the density matrix [Eqs. (2.6b)],

$$V_x^{\text{TS}}(\mathbf{r}) = \int d\mathbf{r}' \, d\mathbf{r}_1 d\mathbf{r}_2 \chi_0^{-1}(\mathbf{r}; \mathbf{r}'; 0) \chi_0(\mathbf{r}'\mathbf{r}; \mathbf{r}_1\mathbf{r}_2; 0)$$

$$\times V(\mathbf{r}_1, \mathbf{r}_2) n(\mathbf{r}_1, \mathbf{r}_2) [n(\mathbf{r})]^{-1} . \qquad (5.10)$$

This approach may be generalized to the dynamic case of the RPAE in Eq. (5.1). We may then define an equivalent local ladder (L) interaction $V_L(\mathbf{r}_1; \omega)$ according to [Fig. 3(b)]
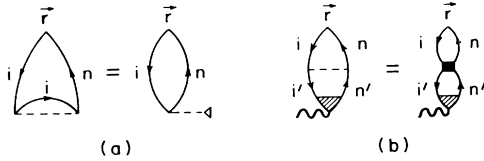

(a)   (b)

FIG. 3. Diagrammatic representation of the averaging procedure for obtaining a local electron-hole interaction. (a) Talman-Shadwick scheme for obtaining a local HF ground-state exchange interaction using the static induced density. (b) Corresponding procedure for obtaining a local ladder interaction from the dynamic induced density.

$$\int d\mathbf{r}_1 \chi_0(\mathbf{r}; \mathbf{r}_1; \omega) V_L(\mathbf{r}_1; \omega) \delta n(\mathbf{r}_1 \omega)$$

$$= - \int d\mathbf{r}_1 d\mathbf{r}_2 \chi_0(\mathbf{r}\mathbf{r}; \mathbf{r}_1\mathbf{r}_2; \omega) V(\mathbf{r}_1, \mathbf{r}_2) \delta n(\mathbf{r}_1\mathbf{r}_2; \omega) \qquad (5.11)$$

or

$$V_L(\mathbf{r}; \omega) = - \int d\mathbf{r}' \, d\mathbf{r}_1 d\mathbf{r}_2 \chi_0^{-1}(\mathbf{r}; \mathbf{r}'; \omega) \chi_0(\mathbf{r}'\mathbf{r}'; \mathbf{r}_1\mathbf{r}_2; \omega)$$

$$\times V(\mathbf{r}_1, \mathbf{r}_2) \delta n(\mathbf{r}_1\mathbf{r}_2; \omega) [\delta n(\mathbf{r}; \omega)]^{-1} , \qquad (5.12)$$

where the frequency-dependent induced densities

$$\delta n(\mathbf{r}_1\mathbf{r}_2; \omega) = \int d\mathbf{r}_3 d\mathbf{r}_4 \chi_0(\mathbf{r}_1\mathbf{r}_2; \mathbf{r}_3\mathbf{r}_4; \omega) v_{\text{eff}}(\mathbf{r}_3, \mathbf{r}_4; \omega) , \qquad (5.13a)$$

$$\delta n(\mathbf{r}_1; \omega) = \delta n(\mathbf{r}_1\mathbf{r}_1; \omega) \qquad (5.13b)$$

enter in the same ways as the density matrix enters in Eq. (5.10). The form of the local ladder interaction therefore is not only *frequency dependent* but also *depends explicitly on the spatial form of the perturbing potential*. Consequently, in principle one first has to solve the problem properly in order to derive a local ladder interaction.

With this local ladder interaction, Eq. (5.1) may be written on local form,

$$v_{\text{eff}}(\mathbf{r}; \omega) = v_{\text{ext}}(\mathbf{r}; \omega) \qquad (5.14a)$$

$$+ \int d\mathbf{r}_1 \left[\int d\mathbf{r}' \, V(\mathbf{r}, \mathbf{r}'; \omega) \chi_0(\mathbf{r}'; \mathbf{r}_1; \omega) \right] v_{\text{eff}}(\mathbf{r}_1; \omega) , \qquad (5.14b)$$

where

$$V(\mathbf{r}_1, \mathbf{r}_2; \omega) = V(\mathbf{r}_1, \mathbf{r}_2) + V_L(\mathbf{r}_1; \omega) \delta(\mathbf{r}_1 - \mathbf{r}_2) . \qquad (5.15)$$

It follows that the local effective interaction potential $v_{\text{eff}}(\mathbf{r}; \omega)$ in Eq. (5.14) may also be written in terms of the induced local density $\delta n(\mathbf{r}; \omega)$ [Eq. (5.13)],

$$v_{\text{eff}}(\mathbf{r}; \omega) = v_{\text{ext}}(\mathbf{r}; \omega) + \int d\mathbf{r}' \, V(\mathbf{r}, \mathbf{r}'; \omega) \delta n(\mathbf{r}'; \omega) . \qquad (5.16)$$

This very simple form is obtained because the Coulomb interaction $V(\mathbf{r}, \mathbf{r}'; \omega)$ now also contains a local, energy-dependent form of the electron-hole (ladder) interaction (5.12).

We note that there is an interesting similarity between the TS local-exchange interaction (5.10) and the local ladder interaction (5.12). The only difference is that the averaging procedure for the Coulomb-exchange interaction in Eq. (5.10) uses the static, ground-state density matrix, while the averaging procedure for the Coulomb-ladder interaction in Eq. (5.12) uses the dynamic, induced-density matrix. If these forms are numerically similar, the local, dynamic ladder interaction (5.12) may be replaced by the local, static exchange interaction (5.10). Consequently, the local ladder interaction $V_L(\mathbf{r}; \omega)$ may appear as equivalent to a local exchange interaction. We shall continue this discussion in Sec. VI.

VI. INTERMEDIATE REPRESENTATIONS

The nonlocal effective interaction potential $v_{\text{eff}}(\mathbf{r}, \mathbf{r}'; \omega)$ in Eqs. (5.1)–(5.2) is not entirely a sound construction

from a physical point of view, since it compensates for the Hartree self-interaction by introducing a modified, nonlocal, response to the external local field. This nonlocal response then accounts for the full direct electron-hole (ladder) interaction, and making the ladder interaction local [Eq. (5.12)] does not change this conclusion.

We feel that a more physical and natural scheme is to define a final-state effective one-electron *wave function* $|\epsilon_{eff}\rangle$ to take into account the spherically averaged potential from the hole (monopole part of the ladder interaction; cancels the Hartree self-interaction). In this way, the average one-electron potential is (nearly) the same in the initial and final states (see Sec. II and paper I), and the remaining nonspherical part of the ladder interaction term in Eq. (5.1c) will represent only a small perturbation. The effective electron-field interaction $v_{eff}(r;\omega)$ then becomes local (or nearly local)

$$M_{\epsilon i}(\omega) = \langle \epsilon_{eff} | v_{eff}(\mathbf{r};\omega) | i \rangle . \tag{6.1}$$

Although this division is not unique, it roughly means that the bubble diagrams (many-electron polarization effects; density-density correlation) are taken into account by a local effective (screened) interaction $v_{eff}(\mathbf{r};\omega)$, while the ladder diagrams (electron-hole attraction) are taken into account by the one-electron potential $V_i(r)$ (Eq. 2.2). Bound states, Rydberg levels, core excitons, etc. are therefore built into the one-electron response function $\mathcal{X}_0$ in Eq. (4.3).

Let us first consider this representation in the case of the single-channel RPAE. We then define the zeroth-order approximation to describe Hartree-Fock-type one-electron excitation with a core hole in a *frozen* environment. This leads us to ground-state HF wave functions for occupied (hole) levels and to frozen-core HF_{av} V^{N-1} wave functions for empty (particle) levels. With this basis of effective one-electron wave functions $|\epsilon_{eff}\rangle = \phi_{eff}$ only a minor part of the bare (unrelaxed) electron-hole ladder interaction is left,[38] leading to a weakly nonlocal interaction v_{eff}.

However, *relaxation effects* can sometimes become large and have dramatic effects on the photoionization cross section. For instance, in $4d$ ionization of Ba and La,[18,19,22,38] and also of Ce, the region from the $4d$ threshold to about 20 eV above threshold (giant dipole resonance) cannot be described at all without proper inclusion of relaxation effects.

In practice, the simplest approach is to use a relaxed core when calculating excited state wave functions. This has been discussed in detail in paper I, where we explicitly showed the one-electron potentials for the frozen and relaxed $4d^9\epsilon f$ configurations (V^{N-1} potentials) and for the $4d^{10}\epsilon f$ configuration (V^N potential). From these results one finds that screening (monopole relaxation; spherical contraction) reduces the bare electron-hole (ladder) interaction (Fig. 4) by as much as a factor of 2 *in the inner-well core region*. Alternatively one could say that in the case of a $4d$ hole in Ba, *relaxation effects raise the inner-well region* by more than 1 Ry. This leads to an important *barrier*[38,42,48] in the effective one-electron RPAER and HFR ^1P $4d^9\epsilon f$ V^{N-1} potentials (R=relaxed), which explains the shape (delayed onset) of the $4d$-ϵf photoioni-
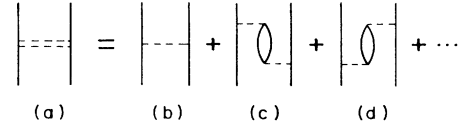
FIG. 4. Diagrammatic description of relaxation through screening of the electron-hole ladder interaction. (a) screened ladder interaction; (b) bare ladder interaction; (c) and (d) lowest-order dynamic screening corrections.

zation cross section in the threshold region.

It should be realized that the effect of relaxation around the $4d$ core hole is really very large. Using a frozen-core HF_{av} basis, going *beyond* the RPAE we would still have a strong ladderlike interaction to account for [monopole screening part of the ladder interaction; Figs. 4(b) and 4(c)]. This would again lead to a strongly nonlocal effective interaction $v_{eff}(\mathbf{r},\mathbf{r}';\omega)$. In a relaxed-core HF_{av} basis the *screened* spherical ladder interaction is effectively taken into account, resulting in weak residual perturbation and a nearly *local* effective interaction $v_{eff}(\mathbf{r},\mathbf{r}';\omega)$.

A useful approach seems to be provided by the LDRPA (local-density random phase approximation).[13,26,38] In paper I we have demonstrated that in the core (inner-well) region the LDA potential is very close to the relaxed $4d^9\epsilon f$ HF_{av} V^{N-1} potential. *An LDA basis therefore approximately incorporates the short-range part of the screened ladder interaction* (there is always a long-range Coulomb tail in a finite system). One then uses an LDA basis of one-electron wave functions to evaluate the RPA equation (off-diagonal bubble diagrams only; self-interaction removed), constructing the charge-density perturbations $\delta n(\mathbf{r};\omega)$ using LDA wave functions. In this way, the induced potential is the classical Coulomb one, and exchange effects are assumed to be taken into account by the choice of basis. The LDRPA approach is described by Eq. (5.14), with $V_L(\mathbf{r}_1;\omega)=0$ in Eq. (5.15), and with a scaled response function to describe the self-interaction free response. Writing the effective ionization matrix element according to

$$\langle \epsilon | v_{eff}(\mathbf{r};\omega) | i \rangle = \langle \epsilon | \mathbf{E} \cdot \hat{\mathbf{r}} \, r_{eff}(\omega) | i \rangle \tag{6.2}$$

(the external field $\mathbf{E}$ is assumed to be homogeneous) we obtain for the effective dipole operator in the LDRPA (Fig. 5)

$$r_{eff}(\omega) = r - \sum_{n,j} c_{nj} \frac{Y_{jn}^1(r)\langle n | r_{eff}(\omega) | j \rangle}{(\omega_{nj}^2 - \omega^2)/2\omega_{nj}} \tag{6.3}$$

with

$$c_{nj} = \tfrac{1}{3}(N_j - \delta_{ij})(2l_n + 1) \begin{bmatrix} l_j & 1 & l_n \\ 0 & 0 & 0 \end{bmatrix}^2 . \tag{6.4}$$

In the radial matrix elements, the wave functions refer to *radial* wave functions. The Kronecker δ-function δ_{ij} (1 if $i=j$; 0 if $i\neq j$) explicitly removes the self-interaction, to prevent that the electron-hole pair to be ionized through the matrix element $\langle \epsilon | r_{eff}(\omega) | i \rangle$ interacts with its own
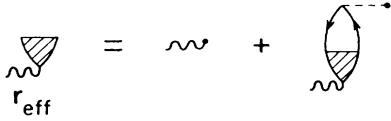
FIG. 5. RPA integral equation for the density response. Produces a realistic response if the one-electron basis set accounts for the average, attractive potential of the core hole (monopole part of the ladder interaction; ionic V^{N-1} potential).

induced field. $Y^1_{jn}(r)$ is the dipole part of the potential defined in Eq. (5.4).

The LDRPA is clearly a hybrid scheme which does not represent any self-consistent approach. In order for this scheme to be equivalent to the RPAE we have to use a HF type of one-electron basis which properly accounts for the electron-hole ladder interaction; in order for the scheme to be equivalent to the self-consistent time-dependent local-density approximation (TDLDA) we have to add a contribution from the density variation of the exchange-correlation potential to the Coulomb potential $Y^1_{jn}(r)$ in Eq. (6.3).

It must be realized that the LDRPA can also be regarded as the first step in a systematic evaluation of the atomic linear response using an LDA basis. Due to physical insight (and comparison with experiment), we may conclude that the LDRPA gives already a very good approximation for the average frequency dependence of the response. However, inclusion of the full residual ladder interaction to infinite order will then account for the long-range part of the atomic potential and introduce the Rydberg-like bound excited states. Moreover, this will lead to a proper description and cancellation of all kinds of self-interaction, meaning that relaxation effects now have to be included explicitly via screening of the ladder interaction.

The LDRPA method may be defined in terms of Eqs. (5.14)—(5.16) for the induced response $\delta n(r;\omega)$ and effective perturbation $v_{\text{eff}}(r_1;\omega)$ by referring the self-interaction corrections to the Coulomb interaction instead of to a scaled response function [Eqs. (6.3) and (6.4)]. In this way, the interaction $V(r_1,r_2;\omega)$ in Eq. (5.15) takes the form

$$V^{\text{LDRPA}}(r_1,r_2;\omega)=V(r_1,r_2)+V_{\text{self}}(r_1,r_2)$$
$$\approx(1-N_j^{-1}\delta_{ij})V(r_1,r_2) . \qquad (6.5)$$

On the other hand, if we consider the TDLDA, the interaction $V(r_1,r_2;\omega)$ in Eq. (5.15) becomes

$$V^{\text{TDLDA}}(r_1,r_2;\omega)=V(r_1,r_2)+V^{\text{TDLDA}}_{\text{xc}}(r_1;\omega)\delta(r_1-r_2) , \qquad (6.6)$$

where the local "ladder" interaction

$$V^{\text{TDLDA}}_{\text{xc}}(r_1;\omega)=-\delta V^{\text{LDA}}_{\text{xc}}/\delta n \qquad (6.7)$$

is the density variation of the exchange-correlation potential. Zangwill and Soven[8,23] used the static limit of Eq. (6.7), while Gross and Kohn[49] recently have derived a fre-

quency dependent interaction. As mentioned before, the equivalent of a short-range screened ladder interaction has been incorporated via the LDA basis. The residual ladder interaction $V^{\text{TDLDA}}_{\text{xc}}(r_1;\omega)$ in Eq. (6.7) is therefore quite weak.

In the same way, one could also consider a time-dependent Talman-Shadwick approximation (TDTSA), which should represent the closest approximation to the RPAE that gives a local induced density $\delta n(r;\omega)$ and a local effective interaction $v_{\text{eff}}(r;\omega)$. The Talman-Shadwick scheme provides an optimal orbital-independent local form $V^{\text{TS}}_x(r)$ of the ground-state HF exchange potential, resulting in a one-electron potential $V^{\text{TS}}(r)$ with a Coulomb tail. This ground-state potential may then be used for calculating a complete set of ground- and excited-state one-electron wave functions and for calculating the response function X_0 [Eq. (4.3)] which appears in Eq. (5.14). Since $V^{\text{TS}}_x(r)$ is orbital independent, in the ground state there can only be partial cancellation of the Hartree self-interaction in the core region.[38] Therefore the TS potential $V^{\text{TS}}(r)$ should be similar to the relaxed HF_{av} V^{N-1} potential everywhere, and similar to the LDA potential in the core region (but with a Coulomb tail at large distances).[38]

The interaction $V(r_1,r_2;\omega)$ in Eqs. (5.14)—(5.15) is given by

$$V^{\text{TDTSA}}(r_1,r_2;\omega)=V(r_1,r_2)+V^{\text{TDTSA}}_x(r_1;\omega)\delta(r_1-r_2) , \qquad (6.8)$$

where the local ladder interaction is determined by the density variation of the local exchange potential

$$V^{\text{TDTSA}}_x(r_1;\omega)=-\delta V^{\text{TS}}_x/\delta n . \qquad (6.9)$$

Since the equivalent of a screened ladder interaction has been taken into account via the TS basis wave functions, the residual local ladder interaction (6.9) must be quite weak. A diagrammatic analysis suggests that the essential ladder contribution is the one that removes the self-terms of the RPA bubble diagrams. This leads us to believe that a Talman-Shadwick based RPA scheme (TSRPA), in analogy with the LDRPA in Eq. (6.5), should be a useful scheme for describing both discrete and continuum excitations in atomic systems.

Finally, for comparison we also give the corresponding expressions for the RPAE with the local form $V^{\text{RPAE}}_L(r_1;\omega)$ [Eqs. (5.12)—(5.16)] of the bare ladder interaction [Fig. 4(b)] and the local form $W^{\text{RPAER}}_L(r_1;\omega)$ of the screened (relaxed) ladder interaction [Fig. 4(a)],

$$V^{\text{RPAE}}(r_1,r_2;\omega)=V(r_1,r_2)+V^{\text{RPAE}}_L(r_1;\omega)\delta(r_1-r_2) , \qquad (6.10)$$

$$V^{\text{RPAER}}(r_1,r_2;\omega)=V(r_1,r_2)+W^{\text{RPAER}}_L(r_1;\omega)\delta(r_1-r_2) , \qquad (6.11)$$

where

$$W^{\text{RPAER}}_L(r_1;\omega)=V^{\text{RPAER}}_L(r_1;\omega)+V^{\text{SCR}}_L(r_1;\omega) . \qquad (6.12)$$

The precise definition of $V(r_1,r_2;\omega)$ depends on the zeroth-order response function X_0. If we work with a

frozen HF_{av} V^{N-1} type of basis sets, the residual (local) *bare* ladder interaction $V_L^{RPAE}(r_1;\omega)$ will be small. However, this is not a good point to break off at, since we know that relaxation effects can be important, and ladder diagrams containing the screening correction $V_L^{SCR}(r_1;\omega)$ [Fig. 4(c) and 4(d)] remain to be included. If instead we work with a *relaxed* HF_{av} V^{N-1} type of basis sets, the static part of the residual (local) *screened* ladder interaction $W_L^{RPAER}(r_1;\omega)$ will be small, and the mean-field description may be greatly improved.

In conclusion, performing the RPA (Fig. 5) with a frozen or relaxed HF_{av} V^{N-1} type of basis gives a local induced response and a good description of the dynamics of many-electron screening in atomic systems.

VII. DIPOLE-LENGTH–DIPOLE-VELOCITY FORMULATIONS OF PHOTOIONIZATION

A. Operator dependence of the effective wave functions

The form of the effective wave function $\phi_\epsilon^{eff}(r)$ in Eq. (4.7) was derived under the assumption that $v_{ext}(r;\omega)$ is an ordinary function of r like $E\cdot r$, and not any operator like $A\cdot p$ (A is the vector potential and p the electron momentum). However, the distinction is crucial: In our formulation it will lead to *operator-dependent forms of the effective wave function and potential.*

In the following we shall work with the radial wave functions and operators, and $\langle \;| \;|\; \rangle$ will denote radial matrix elements. The matrix elements of the length (L) and velocity (V) -dipole operators are defined according to

$$d_{\epsilon i}^L = \langle \epsilon | d^L | i \rangle \;, \tag{7.1a}$$

$$d_{\epsilon i}^V = \langle \epsilon | d^V | i \rangle \;, \tag{7.1b}$$

where

$$d^L = r \;, \tag{7.2a}$$

$$d^V = d/dr \pm l_> /r \;. \tag{7.2b}$$

In Eq. (7.2b), the $+$ sign is to be chosen for the $l \rightarrow l+1$ transition and the $-$ sign for the $l \rightarrow l-1$ transition. $l_>$ is the larger of the angular momenta for the initial- or final-state orbitals.

The photoionization cross section may now be written on the form [α fine-structure constant, a_0 Bohr radius, $c_{\epsilon i}$ from (6.4)]

$$\sigma(\omega) = 4\pi^2 \alpha a_0^2 \omega c_{\epsilon i} |d_{\epsilon i}(\omega)|^2 \;, \tag{7.3}$$

where

$$d_{\epsilon i}(\omega) = \begin{cases} d_{\epsilon i}^L(\omega) & \text{for dipole length } (L) \quad\; (7.4a) \\ \omega^{-1} d_{\epsilon i}^V(\omega) & \text{for dipole velocity } (V) \;. \;\; (7.4b) \end{cases}$$

The RPAE equations for the dipole matrix elements have the form [see Fig. 1(d); cf. Sec. IV and Eqs. (4.9)–(4.15)]

$Nd_{\epsilon i}^L(\omega)$

$$= d_{\epsilon i}^L - P \sum_n \left[\frac{V_{\epsilon n}(\omega)d_{ni}^L}{\omega_n - \omega} + \frac{G_{\epsilon n}(\omega)d_{in}^L}{\omega_n + \omega} \right] \tag{7.5a}$$

$$= d_{\epsilon i}^L - P \sum_n [I_{\epsilon n}^>(\omega)d_{ni}^L + I_{\epsilon n}^<(\omega)d_{in}^L] \;, \tag{7.5b}$$

$Nd_{\epsilon i}^V(\omega)$

$$= d_{\epsilon i}^V - P \sum_n \left[\frac{V_{\epsilon n}(\omega)d_{ni}^V}{\omega_n - \omega} + \frac{G_{\epsilon n}(\omega)d_{in}^V}{\omega_n + \omega} \right] \tag{7.6a}$$

$$= d_{\epsilon i}^V - P \sum_n [I_{\epsilon n}^>(\omega)d_{ni}^V + I_{\epsilon n}^<(\omega)d_{in}^V] \;. \tag{7.6b}$$

Using the properties of the zeroth-order one-electron basis functions we have

$$d_{in}^L = d_{ni}^L \;, \tag{7.7a}$$

$$d_{in}^V = -d_{ni}^V \;, \tag{7.7b}$$

Eq. (7.7b) is strictly true only if the occupied and empty states have been calculated with the same one-electron potential. In the case of the present self-energy corrected HF average basis, Eq. (7.7b) is approximate but fulfilled with good numerical accuracy. The RPAE equations (7.5) and (7.6) may then be rewritten according to

$$Nd_{\epsilon i}^L(\omega) = d_{\epsilon i}^L - P \sum_n [I_{\epsilon n}^>(\omega) + I_{\epsilon n}^<(\omega)]d_{ni}^L \;, \tag{7.8}$$

$$Nd_{\epsilon i}^V(\omega) = d_{\epsilon i}^V - P \sum_n [I_{\epsilon n}^>(\omega) - I_{\epsilon n}^<(\omega)]d_{ni}^V \;. \tag{7.9}$$

The velocity formulation in Eq. (7.9) now has a form closely similar to the length formulation in Eq. (7.8). We can therefore derive an effective radial wave function also in the dipole-velocity case,

$$Nu_\epsilon^{effL}(r) = u_\epsilon(r) - P \sum_n [I_{\epsilon n}^>(\omega) + I_{\epsilon n}^<(\omega)]u_n(r) \;, \tag{7.10}$$

$$Nu_\epsilon^{effV}(r) = u_\epsilon(r) - P \sum_n [I_{\epsilon n}^>(\omega) - I_{\epsilon n}^<(\omega)]u_n(r) \;. \tag{7.11}$$

We have here formulated the RPA(E) in terms of a *single effective wave function* (L or V) *including ground-state correlations.* As a consequence, we have to pay for this by a *operator dependence of the effective wave function.*

We now introduce the definitions

$$|\epsilon_{TDAE}\rangle = N^{-1} \left[u_\epsilon(r) - \sum_n I_{\epsilon n}^>(\omega)u_n(r) \right] \tag{7.12a}$$

$$\equiv |\epsilon_{HF}{}^1P\rangle \;, \tag{7.12b}$$

$$|\epsilon_{corr}\rangle = -N^{-1} \sum_n I_{\epsilon n}^<(\omega)u_n(r) \;, \tag{7.13}$$

which gives

$$|\epsilon_{RPAEL}\rangle = |\epsilon_{TDAE}\rangle + |\epsilon_{corr}\rangle \;, \tag{7.14}$$

$$|\epsilon_{RPAEV}\rangle = |\epsilon_{TDAE}\rangle - |\epsilon_{corr}\rangle \;. \tag{7.15}$$

Applying the Schrödinger equation in reverse [Eq. (2.11)] to the wave functions in Eqs. (7.14) and (7.15) we obtain the corresponding effective potential. An example is shown in Fig. 6 for continuum d levels in Kr in the case of $4p$-ϵd transitions close to threshold ($\epsilon = 0.1$ Ry). Clearly, the effect of ground-state (initial-state) correlations with in the RPA(E) is quite dramatic.

From the properties of the RPAE we have that[3]

$$d_{\epsilon i}^{\text{RPAE}}(\omega) = \langle \epsilon_{\text{RPAEL}} | d^L | i \rangle \qquad (7.16a)$$

$$= \omega^{-1} \langle \epsilon_{\text{RPAEV}} | d^V | i \rangle , \qquad (7.16b)$$

which allows us to write the RPAE dipole matrix element, using Eqs. (7.12)–(7.13), according to

$$d_{\epsilon i}^{\text{RPAE}}(\omega) = \tfrac{1}{2} \langle \epsilon_{\text{TDAE}} | d^L + \omega^{-1} d^V | i \rangle \qquad (7.17a)$$

$$+ \tfrac{1}{2} \langle \epsilon_{\text{corr}} | d^L - \omega^{-1} d^V | i \rangle , \qquad (7.17b)$$

Eq. (7.17) represents a separation of the RPAE dipole matrix element into an average length-velocity part involving HF ^1P (TDAE) final-state wave functions, and a correction describing ground-state correlation.

We now rewrite Eq. (7.17) according to

$$d_{\epsilon i}^{\text{RPAE}}(\omega) = d_{\epsilon i}^{\text{av,TDAE}}(\omega) + \Delta d_{\epsilon i}(\omega) , \qquad (7.18)$$

where

$$N d_{\epsilon i}^{\text{av,TDAE}}(\omega) = N \tfrac{1}{2} \langle \epsilon_{\text{TDAE}} | d^L + \omega^{-1} d^V | i \rangle$$

$$= d_{\epsilon i}^L - \tfrac{1}{2} P \sum_n I_{\epsilon n}^{\geq}(\omega) d_{ni}^L (1 + \omega_n / \omega) \qquad (7.19a)$$

$$= d_{\epsilon i}^L - \tfrac{1}{2} \omega^{-1} P \sum_n V_{\epsilon n}(\omega) d_{ni}^L \frac{\omega_n + \omega}{\omega_n - \omega} \qquad (7.19b)$$

and

$$N \Delta d_{\epsilon i}(\omega) = N \tfrac{1}{2} \langle \epsilon_{\text{corr}} | d^L - \omega^{-1} d^V | i \rangle$$

$$= -\tfrac{1}{2} \sum_n I_{\epsilon n}^{<}(\omega) d_{ni}^L (1 - \omega_n / \omega) \qquad (7.20a)$$

$$= \tfrac{1}{2} \omega^{-1} \sum_n G_{\epsilon n}(\omega) d_{ni}^L \frac{\omega_n - \omega}{\omega_n + \omega} . \qquad (7.20b)$$
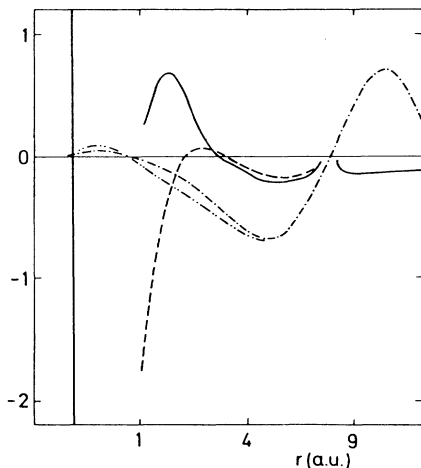

FIG. 6. Effective local ($l=3$) potentials for $4p$-ϵd transitions in Kr calculated in simplified RPAE (SRPAE); $\epsilon = 0.1$ Ry. (———) length, potential; (—·—·—·) length, wave function; (— — —) velocity, potential; (—·· —·) velocity, wave function.

$d_{\epsilon i}^{\text{av,TDAE}}(\omega)$ is the *average length-velocity dipole matrix element in the Hartree-Fock ^1P basis* and $\Delta d_{\epsilon i}(\omega)$ is a correction which leads to the RPAE. The high-frequency behavior of these terms can easily be found. At high frequencies, $G_{\epsilon n}(\omega) \to G_{\epsilon n}$.

In the limit of $\omega \to \infty$ we then have

$$d_{\epsilon i}^{\text{av,TDAE}}(\omega) \to N^{-1} \left[d_{\epsilon i}^L + \tfrac{1}{2} \omega^{-1} \sum_n V_{\epsilon n} d_{ni}^L \right] \qquad (7.21)$$

and

$$\Delta d_{\epsilon i}(\omega) \to -\tfrac{1}{2} N^{-1} \omega^{-1} \sum_n G_{\epsilon n} d_{ni}^L . \qquad (7.22)$$

Since $G_{\epsilon n}$ is roughly factorizable,[5,17] one qualitatively has

$$\sum_n G_{\epsilon n} d_{ni}^L = d_{\epsilon i}^L \sum_n G_{nn} > 0 \qquad (7.23)$$

because the one-electron dipole matrix element $d_{\epsilon i}^L$ is always positive at high energies ϵ, and the diagonal matrix elements G_{nn} of the exchange interaction are also positive.

In a more accurate, numerical, treatment we note that the major contribution to the sum (integral) comes from low energies ω_n. Numerically, for $4d$-ϵf transitions in Ba, we find that $G_{\epsilon n}$ is negative when n lies in the low-energy region and ϵ lies at high energies. Since the one-electron dipole matrix element d_{ni}^L is negative in the low-energy region, the inequality (7.23) is indeed valid. The RPAE dipole matrix element (7.18) (as well as the cross section) therefore lies below the average one at high energies. Moreover, to first order in ω^{-1} there is cancellation (see below) between the interaction terms in Eqs. (7.21) and (7.22), so that the RPAE result, in fact, rapidly tends towards the one-electron result $d_{\epsilon i}^L$.

We can also say something about the general behavior of the correction term (7.20) in the *low-energy region* where the cross section is large and often strongly influenced, or dominated, by collective behavior. Comparing Eq. (7.20b) with the second term in Eq. (7.19b) we note two things: (i) the signs are opposite; (ii) the frequency factors $(\omega_n - \omega)/(\omega_n + \omega)$ and $(\omega_n + \omega)/(\omega_n - \omega)$ are each others inverses and change sign in the same manner; the cancellations in the integrals will therefore be similar. Therefore, since $V_{\epsilon n}(\omega) \approx G_{\epsilon n}(\omega)$ the two contributions beyond the zeroth-order HF_{av} approximation will have similar ω dependence but opposite sign. However, the correction term $\Delta d_{\epsilon i}(\omega)$ in Eq. (7.20b) will have a smaller absolute value and will, roughly speaking, reduce the oscillation of the second term in Eq. (7.19b) around the zeroth-order contribution.

This is further illustrated in Fig. 7, showing photoionization cross sections for the $4p^6$ shell in Kr in the low-energy region. This region is characterized by collective behavior, reflected in the large displacement of oscillator strength relative to the zeroth-order,independent-electron result.[3,8,31] The RPAE cross section σ^{RPAE} (which is quite close to experiment) lies well above σ^{av} in the threshold region, crosses σ^{av} on the high-energy side of the maximum, and then stays well below σ^{av}.

The crossover occurs typically in the region where the continuum oscillator strength begins to fall. In systems which may be described in terms of a collective (giant dipole) resonancelike behavior, similar to the $4d$-f transi-
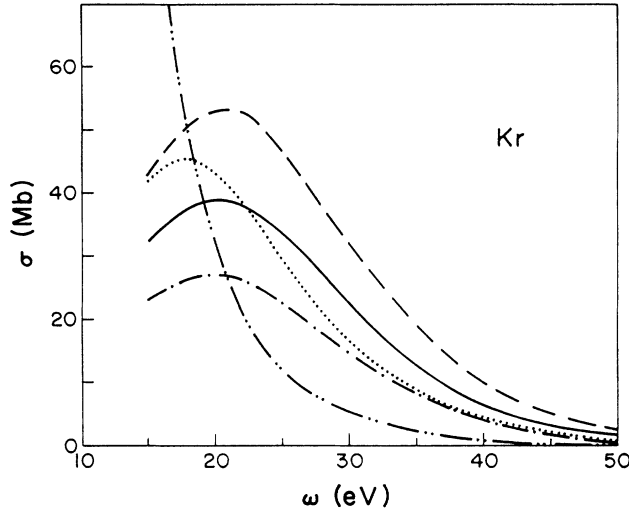
FIG. 7. Photoionization cross sections for $4p$-ϵd transitions in krypton. (— · —) HF$_{av}$, length or velocity; (———) HF ^1P, average length velocity; (— — —) HF ^1P, length; (— · — · —) HF ^1P, velocity; (· · · ·) RPAE.

tions in Xe, Ba, and La, the crossover occurs around the collective resonance energy, which is precisely where the oscillator strength begins to fall. Note that the cases of dramatic differences between HF length and velocity matrix elements and cross sections are indeed associated with systems showing pronounced collective behavior, similar to the outer-shell np^6 cross sections in the rare gases and the inner-shell $4d^{10}$ cross sections in Xe and the surrounding elements.

The fact that the RPAE cross section usually will be closer to the HF ^1P *length* result from threshold towards the maximum in the cross section, and then quite rapidly decrease and become closer to the HF ^1P *velocity* result is of course well known and expected: Here we have only analyzed the reason for this behavior in terms of deviations from an average HF ^1P length-velocity picture.

It must be remembered, however, that even though the RPAE dipole matrix element may be closer to the HF-velocity result at higher energies, the RPAE never tends to the HF ^1P (TDAE) result in any sense because the high-frequency behaviors are qualitatively different: The TDAE matrix element $d_{\epsilon i}^{av,TDAE}(\omega)$ in Eq. (7.21) tends towards the independent-electron limit $d_{\epsilon i}^L$ ($=\omega^{-1}d_{\epsilon i}^V$) as ω^{-1}, and the correlation matrix element $\Delta d_{\epsilon i}(\omega)$ in Eq. (7.22) tends towards zero also as ω^{-1}. However, the sum of these matrix elements, i.e., the RPAE matrix element $d_{\epsilon i}^{RPAE}(\omega)$, tends towards the independent-electron limit $d_{\epsilon i}^L$ as ω^{-2}. To see this, one needs to sum Eq. (7.19) and (7.20) before taking the limit,

$$Nd_{\epsilon i}^{RPAE}(\omega)$$

$$=d_{\epsilon i}^L-P\sum_n \frac{\omega_n}{\omega_n-\omega}[V_{\epsilon n}(\omega)+G_{\epsilon n}(\omega)]d_{ni}^L \quad (7.24a)$$

$$-\tfrac{1}{2}\omega^{-1}P\sum_n \frac{\omega_n^2+\omega^2}{\omega_n^2-\omega^2}[V_{\epsilon n}(\omega)-G_{\epsilon n}(\omega)]d_{ni}^L . \quad (7.24b)$$

Now taking the high-frequency limit, $\omega\to\infty$, we obtain

$$Nd_{\epsilon i}^{RPAE}(\omega)$$

$$=d_{\epsilon i}^L+\omega^{-2}\sum_n \omega_n[V_{\epsilon n}(\omega)+G_{\epsilon n}(\omega)]d_{ni}^L \quad (7.25a)$$

$$+\tfrac{1}{2}\omega^{-1}\sum_n [V_{\epsilon n}(\omega)-G_{\epsilon n}(\omega)]d_{ni}^L . \quad (7.25b)$$

From Eq. (7.16) it also follows that

$$\langle\epsilon_{RPAE}\,|\,d^L-\omega^{-1}d^V\,|\,i\rangle=0 , \quad (7.26)$$

from which we can derive the relation

$$\sum_n [V_{\epsilon n}(\omega)-G_{\epsilon n}(\omega)]d_{ni}^L=0 . \quad (7.27)$$

As a result, due to the well-known interference between the positive and negative frequency contributions (final- and initial-state correlation effects), the RPAE dipole matrix element tends towards the one-electron matrix element such as ω^{-2}. Note that the approximation to set $V_{\epsilon n}(\omega)=G_{\epsilon n}(\omega)$ (simplified RPAE, SRPAE; Refs. 4, 5, 12, 17, 19, and 50) automatically fulfills Eq. (7.27) and gives the correct high-frequency behavior.

We may conclude that it is a meaningless question to ask whether the HF-LS length or velocity (or average length-velocity) formulation is the best at high frequencies, because neither form has the correct frequency dependence.

The average form $\tfrac{1}{2}(d^L+\omega^{-1}d^V)$ of the dipole operator was used by Miller and Dow[51,52] on the grounds that it would lead to better fulfillment of the oscillator sum rule. However, this procedure can be generalized and made more precise: We may state that, as long as we want to arrive at the RPAE, the *form of the dipole operator* is intimately connected with the *form of the effective wave function* for the excited electron. If one starts with the dipole-length operator in Eq. (7.16a) one will have to
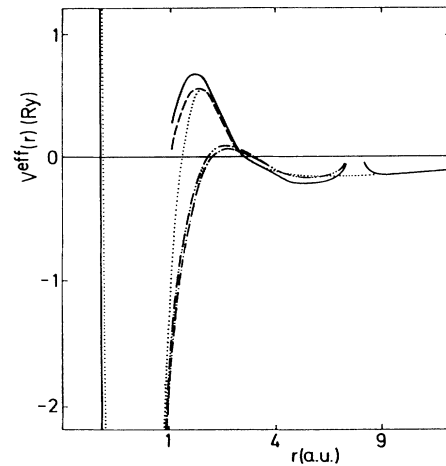

FIG. 8. Effective local ($l=3$) potentials for $4p$-ϵd transitions in Kr. (———) length formulation, SRPAE, $\epsilon=0.1$ Ry; (— — —) length formulation, SRPAE, $\epsilon=0.2$ Ry; (— · — · —) velocity formulation, SRPAE, $\epsilon=0.1$ Ry; (— · — ·) velocity formulation, SRPAE, $\epsilon=0.2$ Ry; (· · · ·) Miller et al. (Ref. 52).

work with the associated RPAE-length wave function (7.10) and potential (Fig. 8). In an analogous manner one could also start from the velocity formulation in Eq. (7.16b), combining the RPAE-velocity dipole operator with the associated wave function (7.11) and potential (Fig. 8). The final RPAE amplitudes and cross sections will be the same.

In the case of the *average dipole-length—dipole-velocity operator*, we cannot use the methods of this section to define an associated wave function that will reproduce the analytical RPAE results. However, we have already noted that when we divide the problem according to Eqs. (7.18)—(7.20), the variation of the correction term $\Delta d_{\epsilon i}(\omega)$ (7.20) will *roughly average to zero* over the relatively low-frequency region which gives the major contribution to the oscillator strength sum rule. Assuming that $\Delta d_{\epsilon i}(\omega)$ in Eq. (7.20) vanishes, the *average* dipole operator in Eq. (7.19) has to be combined with the HF ^1P (TDAE) effective one-electron wave function in Eq. (7.14). This then *approximately* gives the RPAE amplitude and cross section, which agrees quite well with experiment when relaxation effects have been taken into account. In fact, the potential obtained by Miller and Dow,[51,52] (Fig. 8) from fitting theory to experiment turns out[39,40] to be quite close to the HF ^1P V^{N-1} potential,[53] as it should according to the above discussion. Figure 8 rather demonstrates the similarity with the SRPAE-length potential: At low kinetic energies the (S)RPAE and HF ^1P cross sections are quite close and so are the (S)RPAE-length and HF ^1P potentials.[53]

Finally, one should note that the separation in Eq. (7.17) could have been made more general,

$$d_{\epsilon i}^{\mathrm{RPAE}}(\omega) = \tfrac{1}{2}\langle\epsilon_{\mathrm{TDAE}}\,|\,\alpha d^L + (1-\alpha)\omega^{-1}d^V\,|\,i\rangle \qquad (7.28a)$$

$$+ \tfrac{1}{2}\langle\epsilon_{\mathrm{corr}}\,|\,\alpha d^L - (1-\alpha)\omega^{-1}d^V\,|\,i\rangle \ . \qquad (7.28b)$$

One could then determine α by requiring that, e.g., the average cross section $\sigma_{\epsilon i}^{\mathrm{av}}(\omega)$ fulfill the oscillator strength sum rule. However, judging from Fig. 7, this value of α should lie in the vicinity of $\alpha = \tfrac{1}{2}$.

B. Comparison with other theoretical approaches

With the average dipole-length—dipole-velocity operator and the HF ^1P basis, we have a first approximation which roughly fulfills the Thomas-Reiche-Kuhn oscillator strength sum rule. Starting from Eq. (7.19) the average photoionization cross section can be written as (HF=HF ^1P=TDAE)

$$\sigma_{\epsilon i}^{\mathrm{av}}(\omega)$$

$$\propto \omega\,|\,\tfrac{1}{2}\langle\epsilon_{\mathrm{HF}}\,|\,d^L + \omega^{-1}d^V\,|\,i\rangle\,|^2 \qquad (7.29a)$$

$$= \tfrac{1}{2}[\tfrac{1}{2}\omega(\,|\,\langle\epsilon_{\mathrm{HF}}\,|\,d^L\,|\,i\rangle\,|^2 + \omega^{-2}\,|\,\langle\epsilon_{\mathrm{HF}}\,|\,d^V\,|\,i\rangle\,|^2) \qquad (7.29b)$$

$$+ (\,|\,\langle\epsilon_{\mathrm{HF}}\,|\,d^L\,|\,i\rangle\,|\,|\,\langle\epsilon_{\mathrm{HF}}\,|\,d^V\,|\,i\rangle\,|\,)]\ , \qquad (7.29c)$$

or in terms of HF ^1P length and velocity cross sections

$$\sigma_{\epsilon i}^{\mathrm{av}}(\omega) = \tfrac{1}{2}\{\tfrac{1}{2}[\sigma_{\epsilon i}^{\mathrm{HFl}}(\omega) + \sigma_{\epsilon i}^{\mathrm{HFV}}(\omega)] \qquad (7.30a)$$

$$+ [\sigma_{\epsilon i}^{\mathrm{HFl}}(\omega)\sigma_{\epsilon i}^{\mathrm{HFV}}(\omega)]^{1/2}\}\ . \qquad (7.30b)$$

The "truly" average HF ^1P cross section can thus be expressed in terms of the average of the arithmetic (7.30a) and the geometric (7.30b) mean values of the length and velocity HF ^1P cross sections. Since the arithmetic and geometric mean values must be similar, we approximately have

$$\sigma_{\epsilon i}^{\mathrm{av}}(\omega) = \tfrac{1}{2}[\sigma_{\epsilon i}^{\mathrm{HFL}}(\omega) + \sigma_{\epsilon i}^{\mathrm{HFV}}(\omega)] \qquad (7.31a)$$

$$= [\sigma_{\epsilon i}^{\mathrm{HFL}}(\omega)\sigma_{\epsilon i}^{\mathrm{HFV}}(\omega)]^{1/2}\ . \qquad (7.31b)$$

Kelly *et al.*[54] have calculated the $4d$-photoionization cross section of atomic Ba, both with the frozen and relaxed ion core potential, using the geometric mean of the HF ^1P length and velocity cross sections alone in an *ad hoc* manner. They obtained quite reasonable results, although of course distinctly different from the RPAER (relaxed RPAE). From their results[54] one can see that the arithmetic and geometric means indeed give very similar results, and therefore their approach is valid. It should be noted, however, that Eq. (7.31b) has been derived for *partial cross sections*, wile Kelly *et al.*[54] applied the geometric mean formula to the sum of the $l \rightarrow l \pm 1$ cross sections.

VIII. SUMMARY

The general purpose of the present investigation has been to describe the many-electron dynamics of inner-shell excitations in atoms, molecules, and solids in terms of *energy-dependent effective local potentials*. In particular, we want to describe the influence of screening, relaxation and correlation in the core region, i.e., the inner-well region of the atomic potential. The idea is that such potentials eventually may be used as "inner potentials" in solid-state calculations.

In a previous paper[38] we have discussed and compared various one-electron schemes for the ground state and excited states (HF, Slater, LDA, Talman-Shadwick). We also presented numerical results which demonstrated the effects of polarization and relaxation.

In the present paper we have developed a general theoretical framework for describing the photoionization amplitude using dielectric response theory. The major purpose has been to incorporate all many-electron effects (screening of the external perturbation, relaxation, correlation) into an *effective one-electron wave function* for the photoelectron. Acting with the Schrödinger equation in reverse we are then able to derive a *local effective one-electron potential which incorporates many-electron dynamics*. Numerical results of various applications will be presented in a subsequent paper.[53] Some examples have also already been given in a previous paper.[38]

We have also studied an approach where all effects of many-electron interaction are represented in terms of an *effective (screened) electron-photon interaction*. Due to the electron-hole ladder (Hartree) interaction, this effective electron-hole interaction becomes nonlocal (RPAE). We have invented a procedure (related to the Talman-Shadwick scheme) for constructing a local, energy-dependent form of the ladder interaction. RPAE with this local ladder interaction (and with local exchange) should be equivalent to a time-dependent Talman-Shadwick approximation.

Furthermore, we have investigated an intermediate scheme where the average electron-hole ladder interaction (including static relaxation, if desired) is included through an appropriate choice of an effective one-electron wave function. This leaves essentially only the electron-hole bubble interaction (RPA) to be included through a local screened electron-phonon interaction. In one-electron schemes like HF_{av} V^{N-1}, Talman-Shadwick, and LDA, the excited electron effectively sees a full core hole in the core region,[38] which approximately takes care of the ladder interaction. It is therefore meaningful to use RPA schemes based on HF_{av} (SRPAE, simplified RPAE),[4,5,12,17,19,50] on LDA (LDRPA),[13,26] or on a Talman-Shadwick basis (TSRPA). We have defined the LDRPA and discussed the relation to schemes like RPAE, SRPAE, TDLDA, and TDTSA.

It should be mentioned that the similarity between a relaxed HF_{av} V^{N-1} potential and the LDA (or TS) potential only occurs for core excitations from outer and inner valence shells[12,13,25] for which relaxation and self-interaction shifts are comparable.[38] For deeper shells (in Xe and Ba this means $3d$ and deeper) the self-interaction shift is much larger than the relaxation shift[38] and has to be corrected for.[55]

In this paper we have also established relations between the RPAE, on the one hand, and different schemes using average dipole length-velocity formulations on the other. In particular, we find that the average HF ^1P cross section should be defined in terms of an average HF ^1P amplitude based on an average length-velocity dipole operator. The key procedure is the separation of the RPAE one-electron wave function into a final-state TDAE ($=$HF ^1P) part and an initial-state (correlation) part. The RPAE ionization matrix element can then be expressed as the sum of two parts: (i) a TDAE ($=$HF ^1P) matrix element of an *average* dipole-length—dipole-velocity operator, and (ii) a correction in the form of a *difference* dipole-length—dipole-velocity operator evaluated with the correlation part of the photoelectron wave function.

We have demonstrated that the photon energy dependence of the correction term is such that the RPAE cross section lies above the average cross section in the threshold region, and lies below the average cross section at higher photon energies. The crossing typically occurs just above the cross-section maximum where the oscillator strength starts to fall quite rapidly. As a result, the RPAE cross section will typically be closer to the HF ^1P length cross section near threshold and closer to the HF ^1P velocity cross section at somewhat higher energies (above the maximum). However, at high energies the RPAE cross section will tend to the cross section for independent electrons much faster than any HF ^1P (TDAE) scheme (length, velocity, average). This is due to interference between the initial- and final-state interactions in the RPAE, and is provided by the correlation correction to the HF ^1P (TDAE) average amplitude.

In the applications of the present work,[38,53] the potentials have been derived by numerical procedures from numerical wave functions. On the low-energy side of a giant dipole resonance the many-electron modification of the one-electron potential is strongly energy dependent. This energy dependence is necessary for a good description but is difficult to parametrize for solid-state calculations in the low-energy region.

However, the Schrödinger equation can be applied in reverse to the *analytic expression* for the effective one-electron wave function. This results in an *analytic expression for the local effective one-electron potential* in terms of response functions and equivalent quantities. Polarization, relaxation, and correlation effects can then in principle be represented in terms of dynamic contributions to an effective one-electron potential. In particular, it should be possible to extract the energy and space dependence in the form of corrections to an average, static potential. This work is still in progress and will be published separately.

The numerical applications of the present work to Kr, Xe, and Ba will be published separately.[53,56]

APPENDIX

In this Appendix we consider the effective wave function given in Eq. (4.8) at a kinetic energy $\epsilon = \omega + \epsilon_i$. This function can be written in the form

$$u_\epsilon^{eff*}(r) = u_\epsilon(r) -$$

$$- \sum_n \frac{F_{\epsilon n}(\omega) u_n(r)}{\omega_n - \omega - i\delta} - \sum_n \frac{K_{\epsilon n}(\omega) u_n(r)}{\omega_n + \omega}$$

$$= u_\epsilon(r) - P \sum_n \frac{F_{\epsilon n}(\omega) u_n(r)}{\omega_n - \omega} - \sum_n \frac{K_{\epsilon n}(\omega) u_n(r)}{\omega_n + \omega}$$

$$- i\pi F_{\epsilon\epsilon}(\omega) u_\epsilon(r) , \qquad (A1)$$

$P \sum_n$ denotes principle part integration over the continuum. This wave function is a complex quantity and we shall show that it can be written in the form of a real function of r times a complex normalization constant. $F_{\epsilon n}(\omega)$ and $K_{\epsilon n}(\omega)$ satisfy the coupled set of equations

$$F_{\epsilon n}(\omega) = V_{\epsilon n} - \sum_m \frac{F_{\epsilon m}(\omega) V_{mn}}{\omega_m - \omega - i\delta} - \sum_m \frac{K_{\epsilon m}(\omega) G_{mn}}{\omega_m + \omega} ,$$

$$(A2a)$$

$$K_{\epsilon n}(\omega) = G_{\epsilon n} - \sum_m \frac{K_{\epsilon m}(\omega) V_{mn}}{\omega_m + \omega} - \sum_m \frac{F_{\epsilon m}(\omega) G_{mn}}{\omega_m - \omega - i\delta} .$$

$$(A2b)$$

The solution of these equations can be written as

$$F_{\epsilon n}(\omega) = V_{\epsilon n}(\omega)/N^*(\omega) , \qquad (A3a)$$

$$K_{\epsilon n}(\omega) = G_{\epsilon n}(\omega)/N^*(\omega) , \qquad (A3b)$$

which gives a proper normalization of the wave function

$$N^*(\omega) = 1 + i\pi V_{\epsilon\epsilon}(\omega) \qquad (A4)$$

$V_{\epsilon n}(\omega)$ and $G_{\epsilon n}(\omega)$ are reaction matrices

$$V_{\epsilon n}(\omega) = V_{\epsilon n} - P \sum_m \frac{V_{\epsilon m}(\omega) V_{mn}}{\omega_m - \omega} - \sum_m \frac{G_{\epsilon m}(\omega) G_{mn}}{\omega_m + \omega} ,$$

$$(A5a)$$

$$G_{\epsilon n}(\omega) = G_{\epsilon n} - \sum_m \frac{G_{\epsilon m}(\omega) V_{mn}}{\omega_m + \omega} - P \sum_m \frac{V_{\epsilon m}(\omega) G_{mn}}{\omega_m - \omega} .$$

$$(A5b)$$

Inserting Eqs. (A2a) and (A2b) in (A1) gives

$$u_\epsilon^{\text{eff}*}(r) = N^*(\omega)^{-1} \left[u_\epsilon(r) - P \sum_n \frac{V_{\epsilon n}(\omega) u_n(r)}{\omega_n - \omega} \right.$$

$$\left. - \sum_n \frac{G_{\epsilon n}(\omega) u_n(r)}{\omega_n + \omega} \right] \qquad (A6a)$$

$$= P_\epsilon^{\text{eff}}(r) / N^*(\omega) , \qquad (A6b)$$

which is the desired form of the wave function.
Moreover, the following theorem holds.

Theorem. In the RPAE, the effective wave function in a single channel can be written in the form

$$u_\epsilon^{\text{eff}*}(r) = N^*(\omega)^{-1} P_\epsilon^{\text{eff}}(r) , \qquad (A7a)$$

$$N^*(\omega) = 1 + i\pi a_\epsilon , \qquad (A7b)$$

where a_ϵ is a real function of ω and P_ϵ^{eff} is a real function of r and ω if and only if $F_{\epsilon n}(\omega)$ and $K_{\epsilon n}(\omega)$ satisfy the relation

$$F_{\epsilon n}(\omega) + \frac{\omega_n - \omega}{\omega_n + \omega} K_{\epsilon n}(\omega) = a_n [N^*(\omega)]^{-1} , \qquad (A8)$$

where a_n is a real function of ω.

Proof. Equation (A8) is fulfilled in the RPAE, as can be easily verified with the help of Eqs. (A3) to (A5), and we have already shown that in this case the effective wave function can be written in the form (A7). To prove this in an opposite way, we start from Eq. (A1) for the effective wave function. Writing explicitly the real and imaginary parts of the matrices $F_{\epsilon n}(\omega)$ and $K_{\epsilon n}(\omega)$, we obtain the effective wave function in the form

$$u_\epsilon^{\text{eff}*}(r) = I(\omega) Y(r,\omega) - iR(\omega) Z(r,\omega) , \qquad (A9)$$

where

$$Y(r,\omega) = u_\epsilon(r) \left[1 - \frac{\text{Re} K_{\epsilon\epsilon}(\omega)}{2\omega I(\omega)} \right]$$

$$- P \sum_n \frac{u_n(r)}{\omega_n - \omega} \frac{\text{Re} W_{n\epsilon}(\omega)}{I(\omega)} , \qquad (A10a)$$

$$Z(r,\omega) = u_\epsilon(r) \left[1 + \frac{\text{Im} K_{\epsilon\epsilon}(\omega)}{2\omega R(\omega)} \right]$$

$$+ P \sum_n \frac{u_n(r)}{\omega_n - \omega} \frac{\text{Im} W_{n\epsilon}(\omega)}{R(\omega)} , \qquad (A10b)$$

$$I(\omega) = 1 + \pi \, \text{Im} F_{\epsilon\epsilon}(\omega) , \qquad (A10c)$$

$$R(\omega) = \pi \, \text{Re} F_{\epsilon\epsilon}(\omega) , \qquad (A10d)$$

$$\text{Re} W_{n\epsilon}(\omega) = \left[\text{Re} F_{n\epsilon}(\omega) + \frac{\omega_n - \omega}{\omega_n + \omega} \text{Re} K_{n\epsilon}(\omega) \right] , \qquad (A10e)$$

$$\text{Im} W_{n\epsilon}(\omega) = \left[\text{Im} F_{n\epsilon}(\omega) + \frac{\omega_n - \omega}{\omega_n + \omega} \text{Im} K_{n\epsilon}(\omega) \right] . \qquad (A10f)$$

We suppose that the effective wave function is of the form (A7) and we write it as

$$u_\epsilon^{\text{eff}*}(r) = \frac{P_\epsilon^{\text{eff}}(r)}{1 + \pi^2 a_\epsilon^2} - i \frac{\pi a_\epsilon P_\epsilon^{\text{eff}}(r)}{1 + \pi^2 a_\epsilon^2} . \qquad (A11)$$

Comparing the real and imaginary parts of Eqs. (A9) and (A11), we obtain the following relations:

$$\frac{P_\epsilon^{\text{eff}}(r)}{1 + \pi^2 a_\epsilon^2} = I(\omega) Y(r,\omega) , \qquad (A12a)$$

$$\frac{\pi a_\epsilon P_\epsilon^{\text{eff}}(r)}{1 + \pi^2 a_\epsilon^2} = R(\omega) Z(r,\omega) . \qquad (A12b)$$

Equating the r dependent and r independent parts gives

$$P_\epsilon^{\text{eff}}(r) = Y(r,\omega) = Z(r,\omega) , \qquad (A13a)$$

$$\frac{1}{1 + \pi^2 a_\epsilon^2} = I(\omega) , \qquad (A13b)$$

$$\frac{\pi a_\epsilon}{1 + \pi^2 a_\epsilon^2} = R(\omega) . \qquad (A13c)$$

Inserting Eqs. (A10c) and (A10d) into (A13b) and (A13c), we easily find that $F_{\epsilon\epsilon}(\omega)$ has the form

$$F_{\epsilon\epsilon}(\omega) = \frac{a_\epsilon}{1 + i\pi a_\epsilon} , \qquad (A14)$$

which is indeed Eq. (A8) for $n = \epsilon$.

Let us show that Eq. (A8) is satisfied for $n \neq \epsilon$, too. Inserting Eqs. (A10a) and (A10b) into relation (A13a) and taking into account the linear independence of the basis functions $u_n(r)$ we obtain

$$\frac{\text{Re} K_{\epsilon\epsilon}(\omega)}{I(\omega)} = -\frac{\text{Im} K_{\epsilon\epsilon}(\omega)}{R(\omega)} = \text{const} = g_\epsilon , \qquad (A15a)$$

$$\frac{\text{Re} W_{n\epsilon}(\omega)}{I(\omega)} = -\frac{\text{Im} W_{n\epsilon}(\omega)}{R(\omega)} = \text{const} = a_n . \qquad (A15b)$$

Combining Eqs. (A15) with Eqs. (A10c)–(A10f) we obtain

$$K_{\epsilon\epsilon}(\omega) = \frac{g_\epsilon}{1 + i\pi a_\epsilon} , \qquad (A16a)$$

$$F_{n\epsilon}(\omega) + \frac{\omega_n - \omega}{\omega_n + \omega} K_{n\epsilon}(\omega) = \frac{a_n}{1 + i\pi a_\epsilon} , \quad n \neq \epsilon \qquad (A16b)$$

which completes our proof.

Using the method presented above, we are able to calculate the transition process into the discrete state n (photoabsorption case). The effective wave function is given by

Eq. (A6), but the discrete energy ω is displaced versus the zeroth-order energy ω_n and obtained as the solution of the equation

$$\omega - \omega_n - V_{nn}(\omega) = 0 \ .$$ (A17)

The normalization constant N is given as

$$N^2 = 1 + P \sum_n \left[\frac{V_{nn}(\omega)}{\omega_n - \omega} + \frac{G_{nn}(\omega)}{\omega_n + \omega} \right]^2 \ .$$ (A18)

We calculate the norm of the wave function choosing the sign so that the resulting wave function has a positive slope at the origin.

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