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Inelastic processes in extended x-ray-absorption fine structure

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Inelastic processes in extended x-ray-absorption fine structure (EXAFS) are studied using an extension of the semiclassical model of dynamical screening of a core hole and a photoelectron. This treatment effectively includes both *extrinsic* and *intrinsic* inelastic losses, as well as interference between them. The local-density approximation is used to derive a complex, energy-dependent final-state potential which includes dynamical corrections to the static exchange-correlation potential. A local relaxation method is developed to calculate the core-hole Green's function, from which the EXAFS amplitude-reduction factor can be determined. Applications to EXAFS amplitudes for the diatomic molecule Br_2 and for metallic Cu yield results in reasonable agreement with experiment.

I. INTRODUCTION

In a complete treatment of many-electron effects in x-ray-photoemission spectra or in extended x-ray-absorption fine structure (EXAFS) a theory must include both *intrinsic* and *extrinsic* energy losses as well as interference between them. *Extrinsic* processes correspond to the inelastic scattering of the outgoing photoelectron, while *intrinsic processes* involve the relaxation and the excitation of the passive electrons due to the creation of the core hole. Interference effects between the action of the photoelectron and the action of the core hole are expected to become important at low energies when the photoelectron and the core hole are, for a long time, spatially close to each other. In this regime they present a dipole-like object around which the relaxation of the system occurs. To describe the inelastic processes one can use a model Hamiltonian[1,2] $H=H_v+H_{\text{core}}+V_{ch}$, where $H_v=\sum_k \varepsilon_k c_k^\dagger c_k+V_{e\text{-}e}$ is the Hamiltonian for all one-electron states except the core level together with electron-electron interactions, $H_{\text{core}}=\varepsilon_{\text{core}} b^\dagger b$, and $V_{ch}=\sum_{kk'} V_{k,k'}^{ch} c_k^\dagger c_{k'} b b^\dagger$, is the transient core-hole potential. The total absorption can then be expressed[1,2] in terms of two Green's functions, the core-hole Green's function $G_c(t)$ and the transient photoelectron Green's function $G_{k,k'}(t)$:

$$G_c(t)=-i\langle\Phi_0\,|\,T[b(t)b^\dagger(0)]\,|\,\Phi_0\rangle\ , \tag{1}$$

$$G_{k,k'}(t)=-i\frac{\langle\Phi_0'\,|\,T[s(t)c_k(t)c_{k'}^\dagger(0)]\,|\,\Phi_0'\rangle}{\langle\Phi_0'\,|\,s(t)\,|\,\Phi_0'\rangle}\ . \tag{2}$$

Here $|\Phi_0\rangle$ ($|\Phi_0'\rangle$) is the initial (final) many-electron ground state; the core state is occupied in $|\Phi_0\rangle$, and unoccupied in $|\Phi_0'\rangle$; $b, b^\dagger, c_k, c_k^\dagger$ are the creation and annihilation operators for electrons in the core state $|b\rangle$ and in the occupied (i.e., passive or valence) and excited one-particle states $|k\rangle$, respectively; and $c_k(t)=\exp(-iH_v t)c_k\exp(iH_v t)$, $b(t)=\exp(-iHt)b\exp(iHt)$, and $s(t)=\exp(-iH_v t)\exp(iH't)$, where H' is the Hamiltonian with the core hole. Both intrinsic and extrinsic inelastic losses and interference are contained in these two Green's functions. More precisely G_c and $G_{k,k'}$ must be calculated in terms of the time-dependent potential $\phi(t)$ and the self-energy (or exchange-correlation potential) $\Sigma(t)$, which are created by the core hole and photoelectron following photoabsorption, i.e., $G_c=G_c^0+G_c^0\phi_{\text{ind}}(t)G_c$ and $G_{k,k'}=G_{k,k'}^0+G_{k,k'}^0\Sigma(t)G_{k,k'}$. Here we have taken the perturbation to be the induced potential $\phi_{\text{ind}}(t)$ so G_c^0 is the core-hole Green's function calculated in the presence of the core-hole potential V_{ch}, and $G_{k,k'}^0$ is the final-state photoelectron Green's function.[2,3]

Given these two Green's functions, one can write the total absorption cross section $\mu(\omega)$ as a convolution,[1,2]

$$\mu(\omega)=\int d\omega'\mu^{(1)}(\omega-\omega')G_c(\omega')\ , \tag{3}$$

where $\mu^{(1)}(\omega)$ is the single-particle absorption cross section, which is related to the photoelectron Green's function by

$$\mu^{(1)}(\omega)=-\frac{1}{\pi}\text{Im}\sum_{k,k'}\langle b\,|\,\hat{\varepsilon}\cdot\mathbf{r}'\,|\,k\rangle G_{k,k'}(\omega)\langle k'\,|\,\hat{\varepsilon}\cdot\mathbf{r}\,|\,b\rangle\ , \tag{4}$$

$\hat{\varepsilon}$ being the x-ray polarization vector. Similarly, for the EXAFS $\chi(\omega)$, one has[4,5]

$$\chi(\omega)=\int d\omega'\chi^{(1)}(\omega-\omega')G_c(\omega')\ , \tag{5}$$

where $\chi^{(1)}(\omega)$ is the single-particle EXAFS spectrum, i.e., the oscillatory part of $\mu^{(1)}(\omega)$ normalized by the smooth atomic background $\mu^a(\omega)$: $\chi^{(1)}(\omega)=[\mu^{(1)}(\omega)-\mu^a(\omega)]/\mu^a(\omega)$.

The theory of inelastic losses and interference effects in photoemission from solids has been extensively studied (see, for example, the papers of Chang and Langreth[6]). A unified treatment based on a model Hamiltonian similar to that used here has been given by Bardyszewski and Hedin.[7] However, previous calculations of EXAFS in atoms and molecules have been carried out only using *static* exchange-correlations potentials for the photoelectron final state. Such potentials are constructed using a local density approximation (LDA) for the electron self-energy operator[8] and have been applied to calculations of the backscattering amplitudes for many elements.[8,9] In those calculations the extrinsic loss was included only for the photoelectron in the backscattering atom, and dynamical effects were ignored. Thus an additional overall reduction factor had to be introduced to achieve reasonable agreement between the theoretical calculations and experimental results. This reduction factor roughly accounts for both the intrinsic and extrinsic losses in the central absorbing atom. A more detailed theory[4,5] for the effects of intrinsic losses in EXAFS was formulated in terms of the core-hole Green's function and yields an energy-dependent reduction factor $A(k)$ for the EXAFS spectrum given by

$$A(k)=\int_0^{k^2/2} d\omega\, G_c(\omega)\exp[2iR(k_\omega-k)]\Big/\int_0^{k^2/2} d\omega\, G_c(\omega)\ . \tag{6}$$

Here R is the near-neighbor atomic distance and $k_\omega=(k^2-2\omega)^{1/2}$ is the shifted wave number. With both intrinsic and extrinsic losses considered, $\chi(k)$ can be rewritten in terms of a many-body amplitude-reduction factor $S(k)$ as

$$\chi(k)=\frac{-S(k)\,|f_\pi(k)|}{kR^2}\sin(2kR+\phi_k)e^{-2k^2\sigma^2}\ , \tag{7}$$

$$S(k)=-A(k)\exp[-\mathrm{Im}(\delta_1^{\mathrm{out}}+\delta_1^{\mathrm{in}})]\ . \tag{8}$$

Here δ_1^{out} and δ_1^{in} are central atom p-wave scattering phase shifts: one from the path along which the photoelectron goes out of the atom while the other is from the path, later in time, along which the photoelectron is scattered back; $f_\pi(k)$ is the backscattering amplitude of the neighboring atom, ϕ_k is the sum of the real parts of the central atomic phase shifts and the phase of $f_\pi(k)$, and $\exp(-2k^2\sigma^2)$ is the Debye-Waller factor, σ being the rms bond vibrational amplitude. Calculations[5] of $A(k)$ for Br_2 were carried out[4] based on the sudden approximation and Hartree-Fock wave functions. However, an important factor ignored by the sudden approximation is the dynamical or interference effect, which had to be added in an *ad hoc* way.[10]

A goal of this paper is to treat dynamical effects in EXAFS based on a more fundamental theory and to evaluate all the dominant inelastic losses in the EXAFS amplitude. Our approach is adapted from the semiclassical model of dynamical screening applied to a core hole and a photoelectron in a homogeneous electron gas.[11] In this model both the photoelectron and the core hole are treated as point charges; their motion produces a time-dependent potential $\phi(t)$ as well as a time-dependent exchange-correlation potential $\Sigma(t)$.[12–15] Applications of this theory have been made previously both to EXAFS and photoemission in *homogeneous* electron systems.[16,17] Another goal of our work is to introduce efficient approximations for these dynamical effects in inhomogeneous systems. To do this we use the LDA to obtain a dynamical correction to the exchange-correlation potential. A classical trajectory and Wentzel-Kramers-Brillouin-Jeffreys (WKBJ) formula are then used to approximate the dynamical corrections to the atomic scattering phase shifts. Also a new, local relaxation method is developed to obtain the core-hole Green's function for inhomogeneous systems. With this framework, all the ingredients in the overall EXAFS reduction factor $S(k)$ of Eq. (8) can be evaluated.

The outline of this paper is as follows: In Sec. II we briefly review the semiclassical model of dynamical screening and, in Sec. III, we discuss its adaptation to inhomogeneous electron systems. In Sec. IV we evaluate the EXAFS amplitude-reduction factor for Br_2. Dynamical effects are discussed and the contributions to the amplitude factor are calculated and compared with experiment and with other calculations. In Sec. V the reduction factor for metallic Cu is calculated and compared with experiment. Section VI contains a summary and conclusions. Throughout this paper we use atomic units: $\hbar=m_e=e=1$; distance, 1 bohr=0.529 Å; and energy, 1 hartree=27.2 eV.

II. SEMICLASSICAL MODEL OF DYNAMICAL RELAXATION

The semiclassical model of dynamical screening in photoabsorption[11] is based on linear-response theory applied to two point charges in a homogeneous electron gas, the core hole and the photoelectron; it yields a dynamical exchange-correlation potential for such systems. In this section we briefly summarize the main assumptions and results of this model. (a) Conduction electrons. The conduction electrons are described by a simple jellium model, i.e., by an electron gas with density parameter r_s in a uniform positively charged background. (b) Core hole and photoelectron. The core hole and the outgoing photoelectron are treated as classical point charges. The core hole is assumed to sit at the origin while the photoelectron moves along a classical trajectory $\mathbf{r}=\mathbf{k}t$, where the wave vector $\mathbf{k}$ is related to the photoelectron energy ε_k as $\varepsilon_k=k^2/2$. If $t=0$ is time when the core hole and the photoelectron are created, the bare charge density associated with these two point charges is $\rho_0(\mathbf{r},t)=\Theta(t)[\delta(\mathbf{r})-\delta(\mathbf{r}-\mathbf{k}t)]$. (c) Dynamical relaxation. The dynamical relaxation of electrons around these charges is treated by linear-response theory. Introducing a dielectric function $\epsilon(\mathbf{q},\omega)$ for the electron gas, the induced charge density is $\rho_{\mathrm{ind}}(\mathbf{q},\omega)=\rho_0(\mathbf{q},\omega)[\epsilon^{-1}(\mathbf{q},\omega)-1]$, where $\rho_0(\mathbf{q},\omega)$ is the Fourier transform of the bare charge density $\rho_0(\mathbf{r},t)$. Here the dielectric function $\epsilon(\mathbf{q},\omega)$ is taken to be the one-pole approximation to the RPA result,

$$\frac{1}{\epsilon(\mathbf{q},\omega)}-1=1-\frac{1}{\epsilon(\mathbf{q},0)}\,\frac{\omega_p}{\omega-\omega_p+i\epsilon}\ , \tag{9}$$

where the static term $\epsilon(\mathbf{q},0)$ is the Thomas-Fermi function, i.e., $\epsilon(\mathbf{q},0)=1+\lambda^2/q^2$. This approximation only takes into account the plasmon excitations in the system. (d) Induced potential ϕ_{ind} and self-energy Σ. The induced potential is given by

$$\phi_{\text{ind}}(\mathbf{r},t)=\int\frac{d^3q\,d\omega}{(2\pi)^4}\,\frac{4\pi}{q^2}\rho_0(\mathbf{q},\omega)[\epsilon^{-1}(\mathbf{q},\omega)-1]\times\exp(i\mathbf{q}\cdot\mathbf{r}-i\omega t)\ . \tag{10}$$

The self-energy of the photoelectron $\Sigma(t)$ can then be calculated from $\phi_{\text{ind}}(\mathbf{r},t)$ as

$$\begin{aligned}\Sigma(t)&=-\tfrac{1}{2}\int d^3r\,\phi_{\text{ind}}(\mathbf{r},t)\delta(\mathbf{r},\mathbf{k}t)\\&=-\tfrac{1}{2}\phi_{\text{ind}}(\mathbf{k}t,t)=\Sigma_s+\Sigma_d(t)\ ,\end{aligned} \tag{11}$$

which consists of two parts, a static part Σ_s, and a time-dependent, dynamical part $\Sigma_d(t)$. Using the approximation in Eq. (9), the explicit expressions for these two terms are

$$\begin{aligned}\Sigma_s=&-(\omega_p/2k)\tan^{-1}(\lambda k/\omega_p)\\&-i(\omega_p/4k)\ln[1+(\lambda^2k^2/\omega_p^2)]\ ,\end{aligned} \tag{12a}$$

$$\begin{aligned}\Sigma_d(t)=&-\cos(\omega_p t)\left[\frac{1-e^{-\lambda kt}}{2kt}-\frac{\lambda\omega_p^2}{2}I_1(t)\right]\\&+\frac{k\omega_p\lambda^2}{2}\sin(\omega_p t)I_2(t)\\&+i\left[\sin(\omega_p t)\left[\frac{1-e^{-\lambda kt}}{2kt}-\frac{\lambda\omega_p^2}{2}I_1(t)\right]\right.\\&\left.\quad+\frac{k\omega_p\lambda^2}{2}\cos(\omega_p t)I_2(t)\right]\ ,\end{aligned} \tag{12b}$$

where $I_1(t)$ and $I_2(t)$ are given by

$$\begin{aligned}I_1(t)&=\int_0^1 dx\,\frac{e^{-\lambda ktx}}{\omega_p^2+\lambda^2k^2x^2}\ ,\\I_2(t)&=\int_0^1 dx\,\frac{xe^{-\lambda ktx}}{\omega_p^2+\lambda^2k^2x^2}\ .\end{aligned} \tag{13}$$

The static part of the potential Σ_s has been studied previously.[2,12] Its properties[16] are essentially those of the Hedin-Lundquist exchange-correlation potential[9] used, for example, by Lee and Beni,[8] and it gives a good approximation to that potential. The dynamical part $\Sigma_d(t)$ gives corrections to the static potential, and the total potential is reduced from the static part due to the interference effects.

The potentials ϕ_{ind} and Σ can then be used to calculate the Green's functions in Eqs. (1) and (2). The photoelectron Green's function $G_{k,k'}$ can be expressed in terms of complex atomic scattering phase shifts, and accounts for the extrinsic losses. The core-hole Green's function G_c represents the excitation spectrum of the passive electrons in the system[4] and accounts for the intrinsic loss. Both Green's functions contain dynamical or interference terms.

III. LOSSES IN INHOMOGENEOUS SYSTEMS

Calculations[16,17] of the dynamical effects in EXAFS and inelastic losses in photoemission in metals have been carried out for homogeneous electron systems, using the potentials described in Sec. II. In more realistic models one must also include the (atomic) inelastic losses due to the inner-shell electrons. This requires a treatment of the linear response and dynamical relaxation of an inhomogeneous electron system. Our approach[18] is based on the LDA,[19] i.e., the assumption that a nonuniform electron gas behaves locally as a uniform electron gas with the local electron density $\rho(\mathbf{r})$. The LDA for the excited-state exchange-correlation potential $V_{\text{xc}}(\mathbf{r})$ is the electron self-energy Σ of a homogeneous system evaluated at local density $\rho(\mathbf{r})$.[8,20,21] The LDA has also been used for the dielectric function in linear-response theory for inhomogeneous systems. Calculations of the photoabsorption cross section in atoms, made with such dielectric functions and the Thomas-Fermi atomic electron density, give a "universal" photoabsorption curve which agrees roughly with experimental results.[22,23]

In this section we apply the LDA to the semiclassical model of Sec. II. The potentials obtained with this approximation can then be applied to calculations of inelastic losses by the inner-shell electrons. Our approximations are summarized as follows.

(a) LDA for $\Sigma_d(t)$. We use the LDA for both the static and dynamic parts of the exchange-correlation potential [Eq. (12)], $\Sigma(\mathbf{r},t)=\Sigma_s(\rho(\mathbf{r}),p(\mathbf{r}))+\Sigma_d(\rho(\mathbf{r}),p(\mathbf{r}),t)$. Here $\rho(\mathbf{r})$ is local electron density and $p(\mathbf{r})=[k^2+k_F^2(\mathbf{r})]^{1/2}$ is the local electron momentum. The same results for Σ in Eq. (12) can be obtained from direct calculations of linear response in an inhomogeneous electron gas, using the LDA for the dielectric function, i.e., $\epsilon(\mathbf{q},\omega;\mathbf{r})=\epsilon^h(\mathbf{q},\omega;\rho(\mathbf{r}))$. We then use this local dielectric function in Eq. (10) to obtain the induced potential $\phi_{\text{ind}}(\mathbf{r},t)$ and the electron self-energy $\Sigma(\mathbf{r},t)$ at a point $\mathbf{r}$ for a photoelectron at local excited momentum $p(\mathbf{r})$,

$$\phi_{\text{ind}}(\mathbf{r},t)=\int\frac{d^3q\,d\omega}{(2\pi)^4}\,\frac{4\pi}{q^2}\rho_0(\mathbf{q},\omega)[\epsilon^{-1}(\mathbf{q},\omega;\mathbf{r})-1]\times\exp(i\mathbf{q}\cdot\mathbf{r}-i\omega t)\ , \tag{14a}$$

$$\begin{aligned}\Sigma(\mathbf{r},t)&=-\tfrac{1}{2}\int d^3r\,\phi_{\text{ind}}(\mathbf{r},t)\delta(\mathbf{r}-\mathbf{p}(\mathbf{r})t)\\&=-\tfrac{1}{2}\phi_{\text{ind}}(\mathbf{p}(\mathbf{r})t,t)\ .\end{aligned} \tag{14b}$$

(b) Dynamical corrections to atomic phase shifts. To calculate the scattering phase shifts for the photoelectron state using the complex time-dependent exchange-correlation potential, we assume the photoelectron moves along a classical trajectory determined by the time function $t(r)$,

$$t(r)=\int_0^r dr'/p(r')\ . \tag{15}$$

The dynamical corrections to the static atomic scattering phase shifts are then evaluated approximately using the WKBJ method,[17]

$$\delta_l^{\mathrm{dyn}}=\int_{r_0}^{r_{\mathrm{MT}}} dr[k^2-2V(r)-2\Sigma(r,t(r)) -(l+\tfrac{1}{2})^2/r^2]^{1/2} -\int_{r_0'}^{r_{\mathrm{MT}}} dr[k^2-2V(r)-2\Sigma_s(r) -(l+\tfrac{1}{2})^2/r^2]^{1/2}\ , \tag{16}$$

where $V(r)$ is the final-state Coulomb potential in the system in the presence of the core hole, r_{MT} the muffin-tin radius of the atom, and r_0 the "turning point" determined by $k^2=2V(r_0)+2\,\mathrm{Re}\Sigma_s(r_0)+(l+\frac{1}{2})^2/r_0^2$, and similarly for r_0' with Σ_s replacing Σ.

(c) Local relaxation approximation for G_c. We introduce here a new, local relaxation method to calculate the core-hole Green's functions in an inhomogeneous electron system. In this method we treat the passive electrons in each local volume element $\delta v=\delta^3 r$ of the system as a homogeneous electron gas. These local homogeneous regions are assumed to be sufficiently large to relax independently so that the core-hole Green's function can be written as a product of local Green's functions, i.e.,

$$G_c(t)=\prod_{\delta v} g_c^h(\rho(\mathbf{r}),t)\ . \tag{17}$$

Here $g_c^h(\rho(\mathbf{r}),t)$ is the core-hole Green's function in a homogeneous electron system with electron density $\rho(\mathbf{r})$, which is given in terms of ϕ by[17]

$$g_c^h(t)=\exp\left[-i\int_{q\le q_c} d^3q\int_0^t dt'\phi_{\mathrm{ind}}(\mathbf{q},t')\right]\ , \tag{18}$$

where $q_c(r)=\omega_p(r)/k_f(r)$ is the plasmon cutoff wave vector. Substituting (18) into (17), we obtain the following result for G_c for inhomogeneous systems:

$$G_c(t)=\exp\left[-i\int d^3r\, f(r) \times\int_0^t dt'\phi_{\mathrm{ind}}(\rho(\mathbf{r}),\mathbf{r},t')\right]\ , \tag{19}$$

where $f(r)=[\sin(q_c r)-q_c r\cos(q_c r)]/2\pi^2 r^3$. In the limit of a homogeneous system this formula reproduces the exact quantum model results.[24]

IV. INELASTIC EFFECTS IN EXAFS OF $\mathrm{Br_2}$

In this section we use the semiclassical model of Secs. II and III to treat the inelastic effects in the K-shell EXAFS spectrum of the diatomic molecule $\mathrm{Br_2}$. Our calculation is summarized as follows.

(a) Model atomic charge density. We have used the Thomas-Fermi atom[25,26] to approximate the atomic electron charge density $\rho_a(\mathbf{r})$ and the Coulomb potential $V(\mathbf{r})$, which are the basic ingredients in our LDA calculations of the Green's functions. Although the accuracy of the Thomas-Fermi atom is not as good as that, say, from self-consistent atomic codes, it provides a charge density which is probably adequate for the approximate treatment of many-electron effects discussed here.

(b) Calculation of $G_c(t)$ and $A(k)$. The core-hole Green's function $G_c(t)$ is calculated using our local relaxation approximation, Eqs. (17) and (19). Since the overlap between the electron charge densities of the two atoms is small and can be neglected, we simply write $G_c(t)=g_c(\mathbf{0},t)g_c(\mathbf{R},t)$. Here $g_c(\mathbf{0},t)$ is the contribution to G_c from electrons in the central atom,

$$g_c(\mathbf{0},t)=\exp\left[-i\int d^3r\, f(r)\int_0^t dt'\phi_{\mathrm{ind}}(\rho_a(\mathbf{r}),\mathbf{r},t')\right]\ , \tag{20}$$

and $g_c(\mathbf{R},t)$ is the contribution from electrons in the neighboring atom,

$$g_c(\mathbf{R},t)=\exp\left[-i\int d^3r\, f(r)\int_0^t dt'\phi_{\mathrm{ind}}(\rho_a(\mathbf{r}+\mathbf{R}),\mathbf{r},t')\right]\ , \tag{21}$$

where $\rho_a(\mathbf{r})$ is the Br atomic charge density and $|\mathbf{R}|=4.31$ a.u. is the near-neighbor distance in $\mathrm{Br_2}$. The Fourier transform of $G_c(t)$ is given by

$$G_c(\omega)=\int\frac{dt}{2\pi}g_c(t)e^{i\omega t} =\int d\omega' g_c(0,\omega')g_c(\mathbf{R},\omega-\omega')\ . \tag{22}$$

We have calculated $G_c(\omega)$ in (22) numerically, and the result is plotted in Fig. 1. Note, as one expects, that the weight of the high-energy excitation channels are reduced as the kinetic energy of the photoelectron decreases. These dynamical effects are seen to be important at low and moderate energies up to about 500 eV. The reduction factor $A(k)$ due to intrinsic effects is then calculated using Eq. (6). In Fig. 2 we compare our result with two

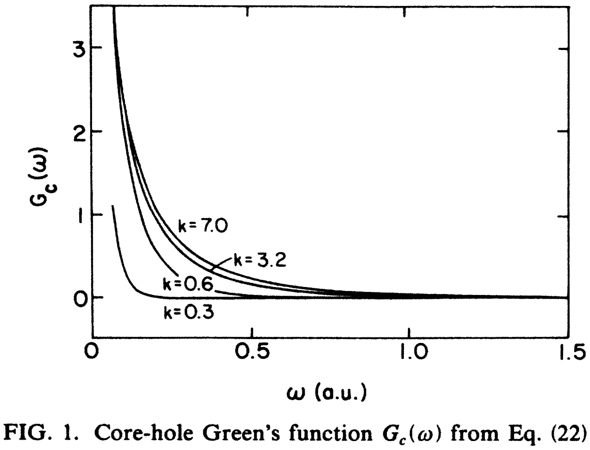

FIG. 1. Core-hole Green's function $G_c(\omega)$ from Eq. (22) for $\mathrm{Br_2}$ for different photoelectron wave numbers.

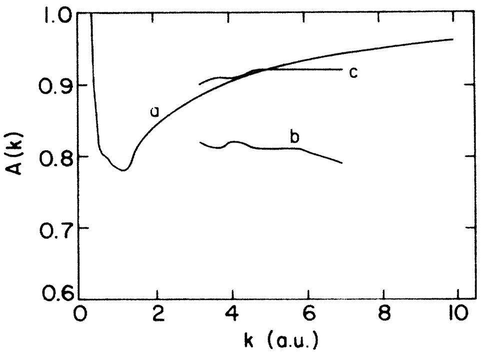

FIG. 2. Amplitude-reduction factor $A(k)$ for Br_2: (a) this theory (b) Hartree-Fock theory (Refs. 5 and 10) and (c) dynamically corrected Hartree-Fock theory (Refs. 5 and 10).

Hartree-Fock (HF) calculations:[5,10] one is the result in the sudden limit (no dynamical effects), the other is that in which an *ad hoc* dynamical correction factor is included. At wave numbers $k > 3.0$ our result is in accord with the dynamical HF calculations.

(c) Central atom phase shifts. To approximate extrinsic losses, the corrections to the p-wave scattering phase shifts of the central atom are evaluated by the WKBJ method of Sec. III. We find that the dynamical correction is only significant for the outgoing path, i.e., for δ_1^{out}. This implies the central atom generally relaxes quickly compared to the transit time. To illustrate this more clearly, we plot in Fig. 3 the dynamical potential of a homogeneous electron system with a typical atomic core charge density ($r_s = 0.5$). Note that the dynamical part of the potential becomes small for $r \geq 3.0$, which is comparable to the muffin-tin radius in Br_2, $r_{\text{MT}} = 2.74$ a.u. Thus the dynamical corrections can be neglected in δ_1^{in}. The phase shift δ_1^{out} is then given (with $l = 1$) by

$$\delta_1^{\text{out}} = \int_{r_1}^{r_{\text{MT}}} dr[k^2-2V(r)-2\Sigma(r,t(r))-(l+\tfrac{1}{2})^2/r^2]^{1/2} - \int_{r_0}^{r_{\text{MT}}} dr[k^2-(l+\tfrac{1}{2})^2/r^2]^{1/2} , \tag{23}$$

and similarly for δ_1^{in} with $\Sigma(r,t(r))$ replaced by $\Sigma_s(r)$. Here $V(r)$ is the Coulomb potential in the central atom with a core hole present, as determined by the Thomas-Fermi equation; Σ and Σ_s are the exchange-correlation potentials with and without dynamical corrections; $t(r)$ is the time function of Eq. (15); and r_0, and r_1, and r_2 are determined by

$$k^2-(l+\tfrac{1}{2})^2/r_0^2=0 , \tag{24a}$$

$$k^2-2V(r_1)-2\,\text{Re}\Sigma(r_1,t(r_1))-(l+\tfrac{1}{2})^2/r_1^2=0 , \tag{24b}$$

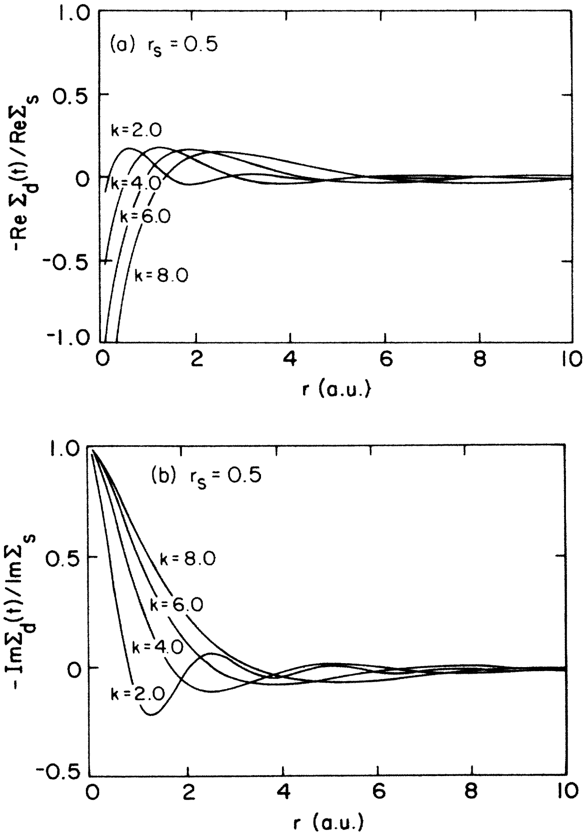

FIG. 3. (a) $-\text{Re}\Sigma_d(t)/\text{Re}\Sigma_s$ for various final-state wave numbers k for a homogeneous electron gas ($r_s = 0.5$); (b) similarly for $-\text{Im}\Sigma_d(t)/\text{Im}\Sigma_s$.

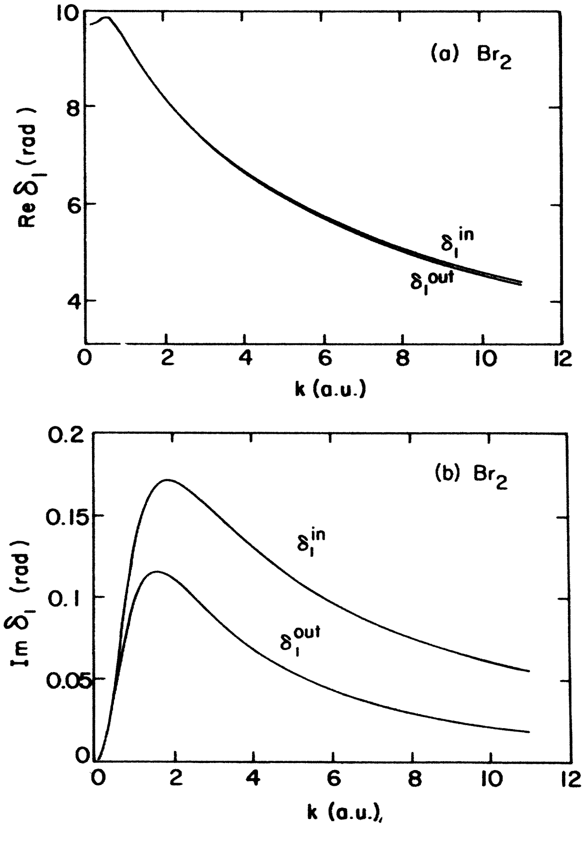

FIG. 4. (a) Real part of the central atom phase shifts $\delta_1^{\text{out}}, \delta_1^{\text{in}}$ for Br_2 calculated using Eq. (15); (b) imaginary parts of $\delta_1^{\text{out}}, \delta_1^{\text{in}}$.

$$k^2-2V(r_2)-\mathrm{Re}\Sigma_s(r_2)-(l+\tfrac{1}{2})^2/r_2^2=0\ . \tag{24c}$$

The numerically calculated phase shifts are plotted in Fig. 4. Note that the dynamical corrections become small at large r, so it is sufficient to use only the static part of Σ in Eq. (12a) for calculations of the backscattering amplitude.

(d) EXAFS amplitude reduction factor $S(k)$. The overall reduction factor $S(k)$ of Eq. (8) can now be calculated. In Fig. 5 our result is compared with experiment[27] and with Hartree-Fock calculations.[10] These results agree reasonably well with each other in the range $k=3.0$–7.0 a.u. An interesting result is that the intrinsic losses compensate for and, for the first shell, almost cancel with the dynamical corrections in the extrinsic losses, i.e., $A(k)\exp(-\mathrm{Im}\delta_1^{\mathrm{dyn}})\cong 1.0$. This suggests that (for the first, and most important, shell) the reduction factor might simply be calculated by the extrinsic losses *without* dynamical corrections, i.e., $S(k)\cong\exp(-2\,\mathrm{Im}\delta_1^{\mathrm{static}})$. Unfortunately this approximation does not work well for the case of Cu, so its general validity is questionable.

(e) Core-hole lifetime effects. The semiclassical model discussed above assumes that the core hole has an infinite lifetime; the validity of this assumption must be examined carefully since the core-hole lifetime is finite, due mostly in this case to Auger transitions. Noguera *et al.* argued[11] that this lifetime is long compared with the typical relaxation time. The effect of a finite lifetime (or energy broadening width Γ) is an additional decay factor $\exp(-\Gamma R/k)$ in $S(k)$. In the case of Br_2 the core-hole broadening width $\Gamma_c=2.1$ eV, as estimated from a linear interpolation of results in Ref. 28. As shown in Fig. 5, this effect is seen to be small, but not negligible.

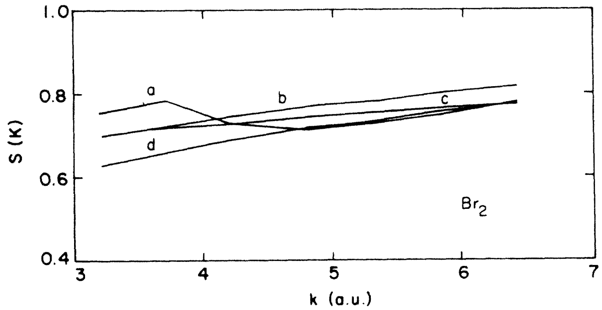

FIG. 5. EXAFS amplitude reduction factor $S(k)$ for Br_2: (a) experiment (Ref. 27) (b) $S(k)$ from Eq. (8) of this work, (c) theory of Ref. 10, and (d) $S(k)$ from this work corrected for core-hole lifetime, i.e., $S(k)\exp(-\Gamma_c R/k)$.

V. INELASTIC EFFECTS IN EXAFS OF Cu

In this section we apply our semiclassical method to study an extended system, metallic Cu. As in Sec. IV we calculate the inelastic losses for the first-shell EXAFS spectrum.

(a) Model charge density. The intrinsic losses in metallic Cu come largely from relaxation of the core electrons in the central atom and from the conduction electrons. Thus we use as a model charge distribution $\rho(r)$, a central atom surrounded by a uniform gas of conduction electrons, i.e.,

$$\rho(r)=\begin{cases}\rho_a(r), & r\le r_0\\ \rho_0, & r>r_0\ .\end{cases} \tag{25}$$

Here $\rho_a(r)$ is the electron charge density in the central atom, and ρ_0 is the charge density of the conduction electrons. The boundary parameter r_0 is chosen so that the charge density is continuous; we find $r_0=2.82$. A more detailed calculation should take into account the effect of the d electrons in neighboring atoms.

(b) Calculation of G_c. By using Eq. (19) and the electron charge density in Eq. (25), the core-hole Green's function $G_c(t)$ is given by

$$G_c(t)=\exp\left[-i\int_{r\le r_0}d^3r\,f(r)\int_0^t dt'\phi_{\mathrm{ind}}(\rho_a(r),\mathbf{r},t')\right]\times\exp\left[-i\int_{r>r_0}d^3r\,f(r)\int_0^t dt'\phi_{\mathrm{ind}}(\rho_0,\mathbf{r},t')\right]=g_c^a(t)g_c^e(t)\ . \tag{26}$$

The two parts, $g_c^a(t)$ and $g_c^e(t)$, represent, respectively, the relaxation of the core electrons in the central atom and the conduction electrons outside. The excitation spectrum is then

$$G_c(\omega)=\int d\omega' g_c^a(\omega')g_c^e(\omega-\omega')\ . \tag{27}$$

The contribution from the conduction electrons $g_c^e(\omega)$ can be expressed as a sum of δ functions at various plasmon excitation energies. i.e.,

$$g_c^e(\omega)=e^{-a_0}\sum_{n=0}^{\infty}\frac{a_0^n}{n!}\delta(\omega-n\omega_p)\ , \tag{28}$$

$$a_0=\frac{1}{\omega_p}\int d^3r\,f(r)\phi_{\mathrm{ind}}(\rho_0,r,t=0)\ .$$

Equation (28) is similar to the core-hole Green's function of the conduction electrons in the quantum electron-plasmon model,[24] which has been used to count the intrinsic losses in photoemission. The modification introduced here with central atomic relaxation included is given by Eq. (27).

(c) Central atom extrinsic losses. The extrinsic losses in the central atom are expressed in terms of the imaginary parts of the p-wave scattering phase shifts δ_1^{out} and δ_1^{in}. Again we use the WKBJ formula of Eq. (22) to ap-

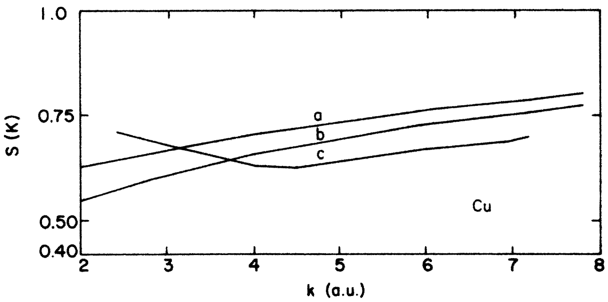

FIG. 6. EXAFS amplitude-reduction factor $S(k)$ for Cu: (a) $S(k)$ from Eq. (8) of this work (b) $S(k)$ from this work corrected for core-hole lifetime, (c) experiment (Ref. 28).

proximate these two imaginary phase shifts. As in the case of Br_2, the dynamical correction for the exchange-correlation potential is only included in the calculation of δ_1^{out}. The muffin-tin radius $r_{\text{MT}}=2.41$ a.u. is half the near-neighbor distance in Cu, $R=4.82$ a.u.

(d) EXAFS reduction factor $S(k)$. Having obtained the core-hole Green's function $G_c(\omega)$ and the central atomic scattering phase shifts $\text{Im}\delta_1$, we can construct the overall EXAFS reduction factor $S(k)$ due to inelastic losses of Eq. (8). This factor is plotted and compared with the experiment[29] in Fig. 6.

(e) Core-hole lifetime effects. For Cu the core-hole lifetime, expressed as an additional broadening energy width, was estimated[28] to be $\Gamma_c \cong 1.5$ eV. To gauge whether this core-hole lifetime is significant, we may express the reduction factor $S(k)$ as an effective broadening energy width Γ_k^{eff}; i.e., $S(k) \equiv \exp(-\Gamma_k^{\text{eff}} R/k)$. With $R=4.82$ a.u. we find that $\Gamma_k^{\text{eff}}=5.4$, 6.6, 7.8, 8.8, 9.5, and 9.8 eV for $k=2$, 3, 4, 5, 6, and 7, respectively. Thus a core-hole lifetime of 1.5 eV is small but not negligible. By adding the core-hole width to the imaginary part of Σ, one obtains even better agreement with experiment in this case (Fig. 6).

VI. SUMMARY AND CONCLUSION

In this paper we have discussed the semiclassical model of dynamical relaxation in photoabsorption and we have presented, as applications, calculations of the many-body amplitude-reduction factors due to inelastic losses in EXAFS. We have introduced several modifications based on the LDA which enable the model to be used for inhomogeneous electron systems. We have also developed a new local relaxation method to calculate the core-hole function directly from the induced potential in an inhomogeneous electron system. To calculate the *extrinsic* losses due to the dynamical (interference) part of the exchange-correlation potential, we have used a time function along the classical trajectory of the photoelectron together with the WKBJ method.

As a first application, the semiclassical model was used to obtain the reduction factor $S(k)$ to the EXAFS amplitude for Br_2. In the range $k > 3.0$ a.u. the results are in reasonable agreement with experiment and with other theoretical calculations based on the Hartree-Fock approximation. Our calculations indicate that dynamical effects are important even at moderate energies, hundreds of eV above threshold. A second application was made to the EXAFS amplitude of metallic Cu. A simple model of the charge density was used to calculate the core-hole Green's function, which only includes the losses from core electrons in the central atom and conduction electrons outside. The result for the amplitude-reduction factor agrees fairly well with experiment. The core-hole lifetime effect is also discussed, and we find that it is small compared with the effective lifetime from the inelastic losses, but not negligible.

In both of these cases we find that the reduction factor $S(k)$ is mainly due to the inelastic losses *inside* the central absorbing atom. The effects from neighboring atoms such as dynamic corrections to the exchange-correlation potentials and intrinsic losses in the core electrons are small compared to those from the central atom. Therefore it is sufficient to use only the central atomic calculations to get a reasonably good reduction factor $S(k)$. Moreover, it is sufficient to use only the static part of the self-energy Σ in calculations of the backscattering amplitude. These findings suggest that dynamical corrections are not very sensitive to the chemical environment.

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