Band-gap enhancement in core-excited metals

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Abstract –Through analyses of the density-matrix equations of motion for electrons in metals, we show that the energy-band gap is *enhanced* when many electrons are excited from core to valence bands, indicating a tendency opposite to the band-gap *reduction* observed in the valence-electron excitation of semiconductors; it is a consequence of inhomogeneous excitation from highly localized core to delocalized valence bands. Such a band-gap enhancement suggests a blue shift of the photoabsorption edge, leading to a possibility of demonstrating saturable absorber switching by means of intense EUV or x-ray free-electron laser pulses.

Introduction. – Photoabsorption spectra of solids in EUV and x-ray regimes exhibit absorption edges, indicating an onset of electron excitation from a localized core band to unoccupied valence or conduction band [1,2]. Recent experiments on near-edge photoabsorption of metals using ultrashort EUV free-electron-laser pulses have demonstrated that, when the intensity of incoming photons exceeds a certain threshold value, saturation of absorption occurs and the photons can penetrate through the sample [3,4]. Such nonlinear transmission phenomena have been reported for L-edge excitation of Al [3] as well as for N-edge excitation of Sn targets [4].

In these experiments, we expect that high-density photoexcited electrons and spatially localized core holes temporarily coexist and interact strongly with each other in the sample while preserving crystalline order; such a novel state of matter may be called a hollow-atom solid [4, 5]. In order to realize a stable hollow-atom solid, we should carefully match the laser wavelength at the edge position so that the excited electrons stay within the conduction band below the vacuum level and rapidly relax through collision with dense conduction electrons. Recent quantum-chemical calculations [5] have indicated an existence of bound states in multiply core-excited lithium clusters when the ionization degree remains small.

The core-excited metal bears a resemblance to the dense electron-hole (e-h) system in a photoexcited semiconductor [6–9]. In the latter case, electrons in the conduction band and holes in the valence band form bound states (i.e., excitons) at low carrier densities, whereas at sufficiently high carrier densities the system turns into a quantum e-h liquid. Theoretically, the mechanism of the transition between exciton gas and e-h liquid phases is attributed to the band-gap reduction [6, 8, 9]; the exchange-correlation effects in strongly interacting electrons and holes give rise to renormalization of the one-electron energies so that the conduction band is lowered and the valence band is elevated as the excitation proceeds.

While the lifetime of e-h liquids in semiconductors can reach a few microseconds [7], deep core holes decay rapidly through the Auger process and hence the lifetime of core-excited metals may be far smaller; it may be on the order of 10 fs in the case of K-shell excitation of lithium [5]. Nevertheless, owing to recent developments of intense x-ray femtosecond laser pulses, it would be possible to induce energy-level shifts within the core-hole lifetime; the resultant ultrafast change in optical constants may be applicable to new nonlinear switching devices for x-rays.

The aim of this work is to examine the energy-gap renormalization in core-excited metals. Due to the localized nature of deep core holes, the theory of homogeneously excited semiconductors with delocalized holes is no longer valid; we derive an expression of energy-gap renormalization for the case of inhomogeneous excitation on the basis of the density-matrix formalism [8–11]. Electron screening is incorporated through the dielectric function of the valence electrons [8,12]. We thus show that the core band is lowered even more drastically than the valence band

and hence the band gap increases as a function of the carrier density, in sharp contrast to the case of e-h liquids in semiconductors.

Theoretical formulation. – Let us consider a solid initially in the ground state, and label its one-electron state by an index k and the corresponding spin index σ. When a time-varying laser field characterized by a vector potential $\boldsymbol{A}(t)$ is applied, electronic transitions occur between these one-electron states. The resultant shift (or renormalization) of the energy levels may be analyzed through the density-matrix formalism [8–11]. We introduce a one-particle density matrix through $\langle\rho_{kk'\sigma}\rangle \equiv \langle c^\dagger_{k\sigma} c_{k'\sigma}\rangle$, where $c^\dagger_{k\sigma}$ and $c_{k\sigma}$ refer to the creation and annihilation operators, respectively, of an electron in state (k,σ); $\langle\cdots\rangle$ denotes an expectation value. Assuming that the nuclei are fixed, the equation of motion for the off-diagonal ($k \neq k'$) density matrix reads [10]

$$
\begin{aligned}
i\hbar\frac{\partial\langle\rho_{kk'\sigma}(t)\rangle}{\partial t} &= (\epsilon^\sigma_{k'} - \epsilon^\sigma_k)\langle\rho_{kk'\sigma}(t)\rangle \\
&+\sum_{k_3}\left[\left(\tilde{\epsilon}^{\mathrm{UHF}}_{k'k_3\sigma}(t) + \frac{e}{m_{\mathrm{e}}c}\boldsymbol{A}(t)\cdot\boldsymbol{p}^\sigma_{k'k_3}\right)\langle\rho_{kk_3}(t)\rangle\right. \\
&\left.-\left(\tilde{\epsilon}^{\mathrm{UHF}}_{k_3k\sigma}(t) + \frac{e}{m_{\mathrm{e}}c}\boldsymbol{A}(t)\cdot\boldsymbol{p}^\sigma_{k_3k}\right)\langle\rho_{k_3k'}(t)\rangle\right] \\
&+i\hbar\left.\frac{\partial\langle\rho_{kk'\sigma}(t)\rangle}{\partial t}\right]_{\mathrm{coll}}.
\end{aligned}
\tag{1}
$$

Here, ϵ^σ_k is the energy of the one-electron state (k,σ) in the unperturbed system ($\mathbf{A}(t) \equiv 0$), which is obtained by the unrestricted Hartree-Fock (UHF) calculation [10]; $\boldsymbol{p}^\sigma_{k'k_3}$ represents the matrix element of the electron momentum operator.

We observe in eq. (1) that the first term on the right-hand side is proportional to $\langle\rho_{kk'\sigma}(t)\rangle$, whose coefficient gives the unperturbed transition energy between states k and k'. Similarly, the second term also contains a quantity proportional to $\langle\rho_{kk'\sigma}(t)\rangle$ and the corresponding coefficient gives rise to the renormalization of the one-electron energies ϵ^σ_k and $\epsilon^\sigma_{k'}$ due to electron excitation. Here,

$$
\begin{aligned}
\tilde{\epsilon}^{\mathrm{UHF}}_{kk'\sigma}(t) = \sum_{k_1k_2\sigma_1} &(V^{\sigma\sigma_1}_{kk'k_1k_2} - \delta_{\sigma\sigma_1}V^{\sigma\sigma}_{kk_2k_1k'}) \\
&\times[\langle\rho_{k_1k_2\sigma_1}(t)\rangle - \delta_{k_1k_2}\delta^{\mathrm{occ}}_{k_1\sigma_1}]
\end{aligned}
\tag{2}
$$

is the self-energy matrix in the UHF approximation [10], where the first and the second terms inside the parentheses represent the Hartree and Fock contributions, respectively;

$$
\begin{aligned}
V^{\sigma\sigma'}_{k_1k_2k_3k_4} = \int d\boldsymbol{r}_1\int &d\boldsymbol{r}_2\psi^{\sigma*}_{k_1}(\boldsymbol{r}_1)\psi^\sigma_{k_2}(\boldsymbol{r}_1)\frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \\
&\times\psi^{\sigma'*}_{k_3}(\boldsymbol{r}_2)\psi^{\sigma'}_{k_4}(\boldsymbol{r}_2)
\end{aligned}
\tag{3}
$$

refers to the electron-electron repulsion integral in terms of the one-electron wavefunctions $\{\psi^\sigma_k(\boldsymbol{r})\}$. The quantity $\delta^{\mathrm{occ}}_{k\sigma}$ is defined in a way such that $\delta^{\mathrm{occ}}_{k\sigma} \equiv 1$ if state (k,σ) is occupied in the initial unperturbed state, and $\delta^{\mathrm{occ}}_{k\sigma} \equiv 0$ if unoccupied. Consequently, the renormalized one-electron energy at time t within the UHF approximation is given as

$$
\tilde{\epsilon}_{k\sigma}(t) = \epsilon^\sigma_k + \tilde{\epsilon}^{\mathrm{UHF}}_{kk\sigma}(t).
\tag{4}
$$

Here, we have omitted the term $(e/m_{\mathrm{e}}c)\boldsymbol{A}(t)\cdot\boldsymbol{p}^\sigma_{kk}$ because it mainly contributes to the intraband transition rate such as the Drude conductivity, which is not the main subject of this work.

In metals, screening by the valence electrons, described by the collision term $\partial\langle\rho_{kk'\sigma}(t)\rangle/\partial t]_{\mathrm{coll}}$ in eq. (1), makes an additional contribution to the energy-level renormalization. To calculate this contribution, we start with the rigorous expression for the collision term,

$$
\begin{aligned}
\left.\frac{\partial\langle\rho_{kk'\sigma}(t)\rangle}{\partial t}\right]_{\mathrm{coll}} = \frac{1}{i\hbar}\sum_{k_1k_2k_3\sigma_1} &[V^{\sigma\sigma_1}_{k'k_3k_1k_2}\delta K^{\sigma\sigma_1}_{kk_3k_1k_2}(t) \\
&-V^{\sigma\sigma_1}_{k_3kk_2k_1}\delta K^{\sigma\sigma_1}_{k_3k'k_2k_1}(t)],
\end{aligned}
\tag{5}
$$

Here, $\delta K^{\sigma\sigma_1}_{kk_3k_1k_2}(t)$ refers to the correlation part of the two-particle density matrix $K^{\sigma\sigma_1}_{kk_3k_1k_2} \equiv \langle c^\dagger_{k\sigma}c^\dagger_{k_1\sigma_1}c_{k_2\sigma_1}c_{k_3\sigma}\rangle$ defined through the relation [9–11],

$$
\begin{aligned}
K^{\sigma\sigma_1}_{kk_3k_1k_2}(t) &= \langle\rho_{kk_3\sigma}(t)\rangle\langle\rho_{k_1k_2\sigma_1}(t)\rangle \\
&-\delta_{\sigma\sigma_1}\langle\rho_{k_1k_3\sigma}(t)\rangle\langle\rho_{kk_2\sigma}(t)\rangle + \delta K^{\sigma\sigma_1}_{kk_3k_1k_2}(t).
\end{aligned}
$$

The Heisenberg equation of motion for $\delta K^{\sigma\sigma_1}_{kk_3k_1k_2}(t)$ is expressed in the form [11]

$$
\begin{aligned}
i\hbar\frac{\partial\delta K^{\sigma\sigma_1}_{kk_3k_1k_2}(t)}{\partial t} &= (\epsilon^\sigma_{k_3} + \epsilon^{\sigma_1}_{k_2} - \epsilon^{\sigma_1}_{k_1} - \epsilon^\sigma_k)\delta K^{\sigma\sigma_1}_{kk_3k_1k_2}(t) \\
&+S^{\sigma\sigma_1}_{kk_3k_1k_2}(t).
\end{aligned}
\tag{6}
$$

By adopting the Born approximation, the last term in eq. (6) may be evaluated as [9]

$$
\begin{aligned}
S^{\sigma\sigma_1}_{kk_3k_1k_2}(t) \approx \sum_{k_4k_5k_6k_7} &V^{\sigma\sigma_1}_{k_4k_5k_6k_7}[\langle\rho_{kk_5\sigma}(t)\rangle\langle\rho_{k_1k_7\sigma_1}(t)\rangle \\
&\times(\langle\rho_{k_6k_2\sigma_1}(t)\rangle - \delta_{k_6k_2})(\langle\rho_{k_4k_3\sigma}(t)\rangle - \delta_{k_4k_3}) \\
&-(\langle\rho_{kk_5\sigma}(t)\rangle - \delta_{kk_5})(\langle\rho_{k_1k_7\sigma_1}(t)\rangle - \delta_{k_1k_7}) \\
&\times\langle\rho_{k_6k_2\sigma_1}(t)\rangle\langle\rho_{k_4k_3\sigma}(t)\rangle] \\
\approx V^{\sigma\sigma_1}_{k_3k'k_2k_1}&\{f_{k_1\sigma_1}(t)[1 - f_{k_2\sigma_1}(t)][1 - f_{k_3\sigma}(t)] \\
&+[1 - f_{k_1\sigma_1}(t)]f_{k_2\sigma_1}(t)f_{k_3\sigma}(t)\}\langle\rho_{kk'\sigma}(t)\rangle.
\end{aligned}
\tag{7}
$$

Here, the diagonal part of the density matrix is denoted as $f_{k\sigma}(t) \equiv \langle\rho_{kk\sigma}(t)\rangle$, which represents the population of state (k,σ). When taking the quadruple summations in eq. (7), we have set $k_5 = k'$ and retained only the term proportional to $\langle\rho_{kk'\sigma}(t)\rangle$ which contributes to the energy-level renormalization; we have also set $k_4 = k_3$, $k_6 = k_2$, and $k_7 = k_1$, so that the diagonal components of the density matrix have been retained as dominant contributions.

Since $f_{k\sigma}(t)$ varies more slowly than $\langle\rho_{kk'\sigma}(t)\rangle$, we may adopt the Markov approximation [8]; the solution to eq.

(6) may then be obtained as

$$\left.\frac{\partial\langle\rho_{kk'\sigma}(t)\rangle}{\partial t}\right]_{\text{coll}} \approx -\frac{1}{i\hbar}\sum_{k_1k_2k_3\sigma_1}\left(\wp\frac{|V^{\sigma\sigma_1}_{k'k_3k_1k_2}|^2}{\epsilon^{\sigma}_{k_3}+\epsilon^{\sigma_1}_{k_2}-\epsilon^{\sigma_1}_{k_1}-\epsilon^{\sigma}_{k}} -\wp\frac{|V^{\sigma\sigma_1}_{kk_3k_1k_2}|^2}{\epsilon^{\sigma}_{k_3}+\epsilon^{\sigma_1}_{k_2}-\epsilon^{\sigma_1}_{k_1}-\epsilon^{\sigma}_{k'}}\right) \times\{f_{k_1\sigma_1}(t)[1-f_{k_2\sigma_1}(t)]+[f_{k_2\sigma_1}(t)-f_{k_1\sigma_1}(t)]f_{k_3\sigma}(t)\} \times\langle\rho_{kk'\sigma}(t)\rangle, \tag{8}$$

where $\wp$ stands for the principal value. Here, the damping factor of the form $-\Gamma\langle\rho_{kk'\sigma}(t)\rangle$, which gives rise to energy-level broadening [10], has been neglected for simplicity. Substitution of eq. (8) into eq. (1) yields the renormalized energy level

$$\tilde{\epsilon}_{k\sigma} = \epsilon^{\sigma}_{k} + \tilde{\epsilon}^{\text{UHF}}_{kk\sigma} + \tilde{\epsilon}^{\text{sc}}_{k\sigma}, \tag{9}$$

with

$$\tilde{\epsilon}^{\text{sc}}_{k\sigma} = -\sum_{k_1k_2k_3\sigma_1(k_1\neq k_2)} |V^{\sigma\sigma_1}_{kk_3k_1k_2}|^2 \times\frac{f_{k_2\sigma_1}-f_{k_1\sigma_1}}{\epsilon^{\sigma_1}_{k_2}-\epsilon^{\sigma_1}_{k_1}}(f_{k_3\sigma}-\delta^{\text{occ}}_{k_3\sigma}) \tag{10}$$

denoting the screening correction within the Born approximation. We make several remarks here: (i) In the denominators on the right-hand side of eq. (8), we have set $\epsilon^{\sigma}_{k_3}-\epsilon^{\sigma}_{k} \approx \epsilon^{\sigma}_{k'}-\epsilon^{\sigma}_{k_3} \approx 0$, which is equivalent to the static-screening approximation [8]; (ii) The factor $f_{k_1\sigma_1}(1-f_{k_2\sigma_1})$ inside the square brackets in eq. (8) has been omitted because it does not contribute to the final result in the examples shown in subsequent sections; (iii) The quantity $\delta^{\text{occ}}_{k_3\sigma}$ has been subtracted in the final term of eq. (10) in order for the energy-level renormalization to be measured from the initial unperturbed state.

Photoexcited semiconductors. – Let us first apply the general formula (9) to the optical excitation of a homogeneous semiconductor to check the validity of the theory. For unperturbed one-electron energies, we adopt simple free-electron-like expressions: $\epsilon^{\sigma}_{\mathbf{k}\mathrm{v}} = -\hbar^2|\boldsymbol{k}|^2/2m_{\mathrm{v}}$ for the valence band (labeled by an index 'v' throughout this section) and $\epsilon^{\sigma}_{\mathbf{k}\mathrm{c}} = \epsilon_{\mathrm{g}} + \hbar^2|\boldsymbol{k}|^2/2m_{\mathrm{c}}$ for the conduction band (labeled by an index 'c'), with m_{v} and m_{c} denoting their respective effective masses. The corresponding one-electron wavefunctions may be expressed as $\psi^{\sigma}_{\mathbf{k}\nu} = \Omega^{-1/2}u_{\nu}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$ ($\nu = \mathrm{v},\mathrm{c}$), where Ω refers to the volume of the system; the Bloch function $u_{\nu}(\mathbf{r})$ has the lattice periodicity and is assumed to be spatially delocalized (i.e., nearly free-electron model). The Coulomb repulsion integrals may then be evaluated as $V^{\sigma\sigma_1}_{\mathbf{k}\nu\mathbf{k_3}\nu\mathbf{k_1}\nu_1\mathbf{k_2}\nu_1} \approx (1/\Omega)v(\mathbf{k}-\mathbf{k_3})\delta_{\mathbf{k}-\mathbf{k_3},\mathbf{k_2}-\mathbf{k_1}}$, where $v(\mathbf{k}) = 4\pi e^2/k^2$ is the Fourier transform of the Coulomb potential. For simplicity, we neglect the interband exchange term and set $V^{\sigma\sigma_1}_{\mathbf{k}\nu\mathbf{k_2}\nu_1\mathbf{k_1}\nu_1\mathbf{k_3}\nu} \approx 0$ for $\nu \neq \nu_1$.

The energy-level renormalizations can then be calculated from eqs. (2) and (10) as

$$\tilde{\epsilon}^{\text{UHF}}_{\mathbf{k}\nu,\mathbf{k}\nu,\sigma} = -\frac{1}{\Omega}\sum_{\mathbf{q}} v(\mathbf{k}-\mathbf{q})(f_{\mathbf{q}\nu\sigma}-\delta^{\text{occ}}_{\mathbf{q}\nu\sigma}), \tag{11}$$

$$\tilde{\epsilon}^{\text{sc}}_{\mathbf{k}\nu,\sigma} = -\frac{1}{\Omega}\sum_{\mathbf{q}} v(\mathbf{k}-\mathbf{q})^2\chi_0(\mathbf{k}-\mathbf{q}) \times(f_{\mathbf{q}\nu\sigma}-\delta^{\text{occ}}_{\mathbf{q}\nu\sigma}), \tag{12}$$

where

$$\chi_0(\mathbf{q}) = \sum_{\nu}\chi^{\nu}_0(\mathbf{q}) = \frac{1}{\Omega}\sum_{\mathbf{k}\nu\sigma}\frac{f_{\mathbf{k+q}\nu\sigma}-f_{\mathbf{k}\nu\sigma}}{\epsilon^{\sigma}_{\mathbf{k+q}\nu}-\epsilon^{\sigma}_{\mathbf{k}\nu}} \tag{13}$$

represents the free-carrier polarizability [8,9,12]. We remark that eq. (11) exposes the exchange contribution; the Hartree contribution vanishes due to the conservation of the total number of electrons, $\sum_{\mathbf{q}\nu_1\sigma_1}(f_{\mathbf{q}\nu_1\sigma_1}-\delta^{\text{occ}}_{\mathbf{q}\nu_1\sigma_1}) = 0$. We also note that eq. (12) can be rewritten in terms of the Hartree-Fock (HF) dielectric function $\epsilon_{\text{HF}}(\mathbf{q})$ through the relation [12], $1/\epsilon_{\text{HF}}(\mathbf{q}) = 1 + v(q)\chi_0(\mathbf{q})$. We may then replace $\epsilon_{\text{HF}}(\mathbf{q})$ by a more accurate dielectric function $\epsilon(\mathbf{q})$ which takes into account e-e correlation beyond HF level [12]. We thus obtain, in the light of eq. (9),

$$\tilde{\epsilon}_{\mathbf{k}\nu,\sigma} = \epsilon^{\sigma}_{\mathbf{k}\nu} - \frac{1}{\Omega}\sum_{\mathbf{q}}\frac{v(\mathbf{k}-\mathbf{q})}{\epsilon(\mathbf{k}-\mathbf{q})}(f_{\mathbf{q}\nu\sigma}-\delta^{\text{occ}}_{\mathbf{q}\nu\sigma}). \tag{14}$$

Equation (14) coincides with the renormalized energy in the screened-exchange approximation [8]. As the electrons are excited from valence to conduction bands, eq. (14) yields $\tilde{\epsilon}_{\mathbf{k}\mathrm{v},\sigma} > \epsilon^{\sigma}_{\mathbf{k}\mathrm{v}}$ and $\tilde{\epsilon}_{\mathbf{k}\mathrm{c},\sigma} < \epsilon^{\sigma}_{\mathbf{k}\mathrm{c}}$, predicting the band-gap reduction, $\tilde{\epsilon}_{\mathrm{g}} \equiv \tilde{\epsilon}_{\mathbf{k}\mathrm{c},\sigma} - \tilde{\epsilon}_{\mathbf{k}\mathrm{v},\sigma} < \epsilon_{\mathrm{g}}$, in qualitative agreement with experiments. To account for the observed energy-gap renormalization more quantitatively, we should additionally incorporate the correlation effect through a treatment of the collision term beyond the Born approximation [6,8]. This is an issue beyond the scope of the present work, however.

Core-excited metals. – We now proceed to the case of core-valence excitation in metals. In this section, the core and the valence bands are labeled by the symbols 'c' and 'v', respectively. We assume that each core electron is strongly localized on a specific atomic site so that its wavefunction is approximated by the corresponding atomic core orbital, $\psi^{\sigma}_{k\mathrm{c}} \approx \phi_{\mathrm{c}}(\mathbf{r}-\mathbf{R}_k)$, where $\mathbf{R}_k$ denotes the position of kth nucleus. When the overlap of adjacent core wavefunctions is negligibly small, we may set $\phi_{\mathrm{c}}(\mathbf{r}-\mathbf{R}_k)\phi_{\mathrm{c}}(\mathbf{r}-\mathbf{R}_{k'}) \approx \delta_{kk'}|\phi_{\mathrm{c}}(\mathbf{r}-\mathbf{R}_k)|^2$, and the unperturbed core-orbital energy may be chosen as $\epsilon^{\sigma}_{k\mathrm{c}} = 0$ independent of k. For the valence band, we adopt the simple plane wave $\psi^{\sigma}_{\mathbf{k}\mathrm{v}} = \Omega^{-1/2}e^{i\mathbf{k}\cdot\mathbf{r}}$ and the free-electron-like energy dispersion, $\epsilon^{\sigma}_{\mathbf{k}\mathrm{v}} = \epsilon_{\mathrm{g}} + \hbar^2|\boldsymbol{k}|^2/2m_{\mathrm{v}}$.

By neglecting core-valence exchange contributions as in the previous section, the Coulomb repulsion integrals (3) may be evaluated as

$$V^{\sigma\sigma_1}_{k\mathrm{c}k_3\mathrm{c}k_1\mathrm{c}k_2\mathrm{c}} = \begin{cases} \delta_{kk_3}\delta_{k_1k_2}U, & k = k_1 \\ \delta_{kk_3}\delta_{k_1k_2}\frac{e^2}{|\mathbf{R}_k-\mathbf{R}_{k_1}|}, & k \neq k_1, \end{cases} \tag{15a}$$

$$V^{\sigma\sigma_1}_{\mathbf{k}\mathrm{v}\mathbf{k_3}\mathrm{v}\mathbf{k_1}\mathrm{v}\mathbf{k_2}\mathrm{v}} \approx \frac{\delta_{\mathbf{k}-\mathbf{k_3},\mathbf{k_2}-\mathbf{k_1}}}{\Omega}v(\mathbf{k}-\mathbf{k_3}), \tag{15b}$$

$$V^{\sigma\sigma_1}_{kck_3\mathrm{c}\mathbf{k_1}\mathrm{v}\mathbf{k_2}\mathrm{v}} \approx \frac{\delta_{kk_3}}{\Omega}|F_\mathrm{c}(\mathbf{k_1}-\mathbf{k_2})|^2 v(\mathbf{k_1}-\mathbf{k_2}) \times e^{-i(\mathbf{k_1}-\mathbf{k_2})\cdot \mathrm{R}_k}. \tag{15c}$$

Here, $U \equiv \int d\boldsymbol{r_1} \int d\boldsymbol{r_2} |\phi_\mathrm{c}(\boldsymbol{r_1})|^2 |\phi_\mathrm{c}(\boldsymbol{r_2})|^2 \frac{e^2}{|\boldsymbol{r_1}-\boldsymbol{r_2}|}$ refers to the on-site Coulomb repulsion energy between electrons in the core orbital, and $F_\mathrm{c}(\mathbf{k}) \equiv \int d\boldsymbol{r} |\phi_\mathrm{c}(\boldsymbol{r})|^2 e^{-i\mathbf{k}\cdot\mathbf{r}}$ denotes the core-electron form factor.

The energy renormalization factors can thus be calculated in light of eqs. (2) and (10) as

$$\begin{aligned}\tilde{\epsilon}^{\mathrm{UHF}}_{k\mathrm{c},k\mathrm{c},\sigma} &= U\sum_{\sigma_1}(1-\delta_{\sigma\sigma_1})(f_{k\mathrm{c}\sigma_1}-1) \\ &+ \sum_{k_1(\neq k),\sigma_1} \frac{e^2}{|\mathbf{R}_k-\mathbf{R}_{k_1}|}(f_{k_1\mathrm{c}\sigma_1}-1) \\ &+\frac{v(0)}{\Omega}\sum_{\mathbf{q}\sigma_1}(f_{\mathbf{q}\mathrm{v}\sigma_1}-\delta^{\mathrm{occ}}_{\mathbf{q}\mathrm{v}\sigma_1}),\end{aligned} \tag{16a}$$

$$\tilde{\epsilon}^{\mathrm{sc}}_{k\mathrm{c},\sigma} = -\frac{1}{\Omega}\sum_{\mathbf{q}}|F_\mathrm{c}(\mathbf{q})|^4 v(\mathbf{q})^2 \chi^{\mathrm{v}}_0(\mathbf{q})(f_{k\mathrm{c}\sigma}-1), \tag{16b}$$

$$\tilde{\epsilon}^{\mathrm{UHF}}_{\mathbf{k}\mathrm{v},\mathbf{k}\mathrm{v},\sigma} = -\frac{1}{\Omega}\sum_{\mathbf{q}} v(\mathbf{k}-\mathbf{q})(f_{\mathbf{q}\mathrm{v}\sigma}-\delta^{\mathrm{occ}}_{\mathbf{q}\mathrm{v}\sigma}), \tag{16c}$$

$$\begin{aligned}\tilde{\epsilon}^{\mathrm{sc}}_{\mathbf{k}\mathrm{v},\sigma} &= -\frac{1}{\Omega}\sum_{\mathbf{q}} v(\mathbf{k}-\mathbf{q})^2 \chi^{\mathrm{v}}_0(\mathbf{k}-\mathbf{q}) \\ &\times(f_{\mathbf{q}\mathrm{v}\sigma}-\delta^{\mathrm{occ}}_{\mathbf{q}\mathrm{v}\sigma}).\end{aligned} \tag{16d}$$

Here, we have used the relations $\delta^{\mathrm{occ}}_{k\mathrm{c}\sigma}=1$ and

$$\sum_{k\sigma}(f_{k\mathrm{c}\sigma}-1)+\sum_{\mathbf{k}\sigma}(f_{\mathbf{k}\mathrm{v}\sigma}-\delta^{\mathrm{occ}}_{\mathbf{k}\mathrm{v}\sigma})=0.$$

Initially, the valence electrons occupy the region $|\mathbf{k}| \leq k_\mathrm{F}$, with $k_\mathrm{F}=(3\pi^2 n_\mathrm{e})^{1/3}$ denoting the Fermi wavenumber. Hence, we consider the case where the core electrons are excited to the valence band within the region $k_\mathrm{F} < |\mathbf{k}| \leq 2^{1/3}k_\mathrm{F}$. To simplify the problem, we introduce an average population $\bar{f}$ $(0 \leq \bar{f} \leq 1)$ and set

$$f_{\mathbf{k}\mathrm{v}\sigma}-\delta^{\mathrm{occ}}_{\mathbf{k}\mathrm{v}\sigma} = \begin{cases} \bar{f}, & k_\mathrm{F} < |\mathbf{k}| \leq 2^{1/3}k_\mathrm{F} \\ 0, & |\mathbf{k}| \leq k_\mathrm{F}\end{cases} \tag{17a}$$

$$f_{k\mathrm{c}\sigma}-1=-\frac{\bar{f}}{2}. \tag{17b}$$

The ansatz (17b) may be valid so long as all the core electrons have the same probability of excitation. When $\bar{f}=1$, half of the core electrons are excited and the valence band is fully occupied; it is possible to excite the remaining core electrons further to higher conduction bands but such a possibility is neglected here.

In accordance with eqs. (9), (16) and (17), the renormalized core and valence energy levels can be expressed in terms of $\bar{f}$ as

$$\begin{aligned}\tilde{\epsilon}_{k\mathrm{c},\sigma} &= -\bar{f}\left(\frac{U}{2}-\alpha_\mathrm{M}\frac{e^2}{a}\right) \\ &+\frac{\bar{f}}{2\Omega}\sum_{\mathbf{q}}|F_\mathrm{c}(\mathbf{q})|^4 v(\mathbf{q})\left[\frac{1}{\epsilon^{\mathrm{v}}(\mathbf{q})}-1\right],\end{aligned} \tag{18a}$$

$$\tilde{\epsilon}_{\mathbf{k}\mathrm{v},\sigma} = \epsilon^{\sigma}_{\mathbf{k}\mathrm{v}} - \frac{\bar{f}}{\Omega}\sum_{\mathbf{q}(k_\mathrm{F}<|\mathbf{q}|\leq 2^{1/3}k_\mathrm{F})}\frac{v(\mathbf{k}-\mathbf{q})}{\epsilon^{\mathrm{v}}(\mathbf{k}-\mathbf{q})}. \tag{18b}$$

In the derivation of eq. (18a), we have made use of the relation

$$\sum_{k_1(\neq k)}\frac{e^2}{|\mathbf{R}_k-\mathbf{R}_{k_1}|}-n_{\mathrm{atom}}v(0)=-\alpha_\mathrm{M}\frac{e^2}{a},$$

where α_M refers to the Madelung constant of the lattice [13], n_{atom} is the atomic number density, and $a=(3/4\pi n_{\mathrm{atom}})^{1/3}$; $\epsilon^{\mathrm{v}}(\mathbf{q})$ is the dielectric function of the valence electrons [12]. It should be noted in eq. (18a) that the Hartree term no longer vanishes since an excitation from localized core to delocalized valence orbitals is highly inhomogeneous.

K-shell excitation of lithium. – As a numerical example, we apply eqs. (18) to K-shell excitation of metallic lithium, for which the observed photoabsorption edge energy is 55 eV [1]. We adopt $\alpha_\mathrm{M}=1.79$ by assuming the body-centered-cubic lattice [13]. The density and effective mass are chosen as $n_{\mathrm{atom}}=4.75\times10^{22}$ cm^{-3} [14] and $m_\mathrm{v}=1.53m_\mathrm{e}$ [15], respectively, where m_e is the bare electron mass. The core wavefunction $\phi_\mathrm{c}(\mathbf{r})$ may be approximated by a Slater-type 1s orbital with exponent $\zeta=2.69$ [10], for which $U=(5/8)\zeta e^2/a_\mathrm{B}$ and $F_\mathrm{c}(\mathbf{q})=16\zeta^4/[4\zeta^2+(qa_\mathrm{B})^2]^2$, with a_B denoting the Bohr radius. The dielectric function of a strongly coupled electron liquid including the Ichimaru-Utsumi local-field correction [12,16] is adopted for $\epsilon^{\mathrm{v}}(\mathbf{q})$, with the electron density $n_\mathrm{e}=n_{\mathrm{atom}}(1+\bar{f})$ and the electron effective mass m_v.

In fig. 1, we plot the energy-level renormalization for the core band, $\Delta\epsilon_\mathrm{c} \equiv \tilde{\epsilon}_{k\mathrm{c},\sigma}$, and that for the valence band, $\Delta\epsilon_\mathrm{v} \equiv (\tilde{\epsilon}_{\mathbf{k}\mathrm{v},\sigma}-\epsilon^{\sigma}_{\mathbf{k}\mathrm{v}})|_{\mathbf{k}=\mathbf{0}}$. It can be found that both the core and the valence bands are lowered ($\Delta\epsilon_\mathrm{c} < \Delta\epsilon_\mathrm{v} < 0$) as $\bar{f}$ increases. The core band is lowered more drastically than the valence band and hence the renormalized band gap $\tilde{\epsilon}_\mathrm{g}$ turns out to be an increasing function of $\bar{f}$, namely, $\tilde{\epsilon}_\mathrm{g} \equiv \epsilon_\mathrm{g}+\Delta\epsilon_\mathrm{v}-\Delta\epsilon_\mathrm{c} > \epsilon_\mathrm{g}$; this trend is opposite to the case of the e-h liquids in semiconductors, $\tilde{\epsilon}_\mathrm{g} < \epsilon_\mathrm{g}$.

The origin of such a band-gap enhancement is attributed to the first term on the right-hand side of eq. (18a), which physically represents the interaction of a core electron with the surrounding core holes and valence carriers; this term takes on a large negative value because of the strong attraction between a core electron and a core hole in the same orbital. The screening by valence electrons, exposed by the second term on the right-hand side of eq. (18a), likewise enhances the band gap. The expression (18b) for the renormalized valence band is similar to eq. (14) except for the difference in the range of $\mathbf{q}$-integrations and the difference between $\epsilon^{\mathrm{v}}(\mathbf{k}-\mathbf{q})$ and $\epsilon(\mathbf{k}-\mathbf{q})$.

In formulae (18), correlation between valence electrons is taken into account through $\epsilon^{\mathrm{v}}(\mathbf{q})$, whereas the e-h interaction is yet treated within the HF level due to our use of the Born approximation in eq. (7). To the author's knowledge, however, an expression for energy-gap renormaliza-

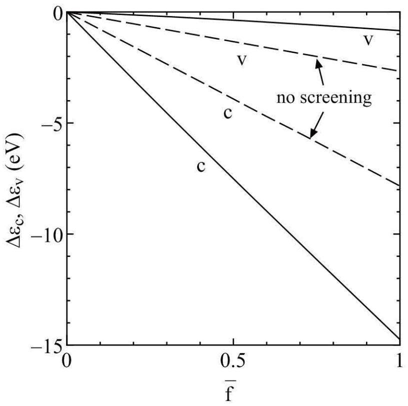

Fig. 1: Renormalization of core (c) and valence (v) band energies in K-shell excited lithium. The solid curves depict the numerical results obtained from eqs. (18); the dashed curves neglect electron screening by setting $\epsilon^{\mathrm{v}}(\mathbf{q}) \equiv 1$.

tion in core-excited metals has not been presented before even within the crude screened-exchange approximation. Rigorous many-body theory of multiple core-valence excitation is a challenging task [17]; it remains to be seen how the large energy-gap enhancement predicted in fig. 1, especially near $\bar{f} \approx 1$, would be modified when the strong e-h correlation beyond the screened-exchange approximation is taken into account [11,17].

Concluding remarks. – On the basis of the density-matrix formalism, we have derived expressions for band-gap renormalization due to core-valence excitation of metals. The screening effect has been incorporated through Born approximation to the electron collision term, where strong correlation between valence electrons has been additionally taken into account through the dielectric function. Validity of the theory has been confirmed for homogeneous e-h liquids in optically excited semiconductors, where the expression based on the static-exchange approximation has been recovered. In the case of an inhomogeneous excitation from a localized flat core band to a delocalized free-electron-like valence band, we have shown that the core band is significantly lowered, leading to a band-gap enhancement; this feature is in sharp contrast to the band-gap reduction in homogeneously excited semiconductors where both the electrons and holes are delocalized.

In the core-electron excitation processes, the concept of final-state interaction is known to be important [18]: The valence electrons respond to the sudden appearance of a core hole and redistribute themselves self-consistently. The redistribution is essentially a many-body effect and described by a set of terms on the right-hand side of eq. (1) other than the leading term. In the present work, the redistribution effect is taken into account only partially because of our use of the screened-exchange approximation and the free-electron-like valence-band model. Clearly, a strong e-h correlation and a realistic crystal structure can both influence the redistribution and the resultant band gap of a real metal. These quantitative considerations will be deferred to a future study.

The sign of the band-gap renormalization is crucial for applications to nonlinear photonic devices [4]. Suppose that a metallic sample is irradiated by a laser pulse with its photon energy E_ν tuned slightly above the edge. When the pulse induces core-electron excitation and enhances the band gap as predicted by the present theory, the absorption edge would shift toward high-energy side above E_ν; we then expect a drastic reduction of the photoabsorption coefficient at E_ν. This mechanism could work as an ultrafast saturable absorber switch for EUV/x-ray photons [4].

* * *

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