I. ENGERGY CORRECTIONS

The exact solution including the relativistic corrections is defined by

$$\left[\hat{H}_0 + \lambda\hat{H}'\right]\phi_{\vec{\nu}} = \varepsilon_{\vec{\nu}}\phi_{\vec{\nu}}, \tag{1}$$

where $\vec{\nu}$ represents the collection of all the quantum numbers. $\hat{H}_0$ is the zeroth order Hamiltonian,

$$\hat{H}_0 = -\frac{1}{2}\nabla^2 + V(r). \tag{2}$$

The function $V(r)$ is the Hartree Fock Slater potential. Let $\phi_{\vec{\nu}}^{(0)}$ and $\varepsilon_{nl}^{(0)}$ be the eigen functions and eigen energies of $\hat{H}_0$,

$$\hat{H}_0\phi_{\vec{\nu}}^{(0)} = \varepsilon_{nl}^{(0)}\phi_{\vec{\nu}}^{(0)}. \tag{3}$$

Note that the the zeroth order eigen energy only depends on n and l. Since the l state has $2(2l+1)$ degeneracy, we work on degenerate perturbation theory. The perturbation series of the exact wave function and energy are given by

$$\phi_{\vec{\nu}} = \varphi_{\vec{\nu}}^{(0)} + \lambda\phi_{\vec{\nu}}^{(1)} + \cdots, \tag{4a}$$

$$\varepsilon_{\vec{\nu}} = \varepsilon_{nl}^{(0)} + \lambda\varepsilon_{\vec{\nu}}^{(1)} + \cdots \tag{4b}$$

We introduce the total angular momentum operator $\hat{j}$,

$$\hat{j} = \hat{l} + \hat{s}, \tag{5}$$

where $\hat{l}$ and $\hat{s}$ are the operator of the orbital and spin augular momentum. We expand the zeroth order wave function $\varphi_{\vec{\nu}}^{(0)}$ in terms of the j coupled basis $\psi_{nljm}^{(0)}$, which is the simaltaneous eigen function of $\hat{j}^2$, $\hat{j}_z$, $\hat{H}_0$, $\hat{l}^2$ and $\hat{s}^2$ operators,

$$\hat{j}^2\psi_{nljm}^{(0)} = j(j+1)\psi_{nljm}^{(0)}, \tag{6a}$$

$$\hat{j}_z\psi_{nljm}^{(0)} = m\psi_{nljm}^{(0)}. \tag{6b}$$

The superscript (0) is added to the function $\psi_{nljm}^{(0)}$ to emphasize that it is also the eigen function of $\hat{H}_0$. The set of the collection of the quantum numbers $\vec{\nu}$ to specify the state is

$$\vec{\nu} = (n, l, j, m). \tag{6c}$$

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The zeroth order wave function $\varphi_{\vec{\nu}}^{(0)}$ is given by

$$\varphi_{\vec{\nu}}^{(0)} = \sum_{j'm'} C_{nlj'm'}^{(0)} \psi_{nlj'm'}^{(0)}. \tag{7}$$

Substituting Eqs. (7) and (4) to Eq. (1), up to the order of λ^1, we obtain

$$(\hat{H}' - \varepsilon_{nljm}^{(1)}) \sum_{j'm'} C_{nlj'm'}^{(0)} \psi_{nlj'm'}^{(0)} + (\hat{H}_0 - \varepsilon_{nljm}^{(0)}) \phi_{nljm}^{(1)} = 0. \tag{8}$$

Multiplying $\psi_{nljm}^{(0)*}$ from the left, and integrating over the space, we obtain,

$$\sum_{j'm'} \left[H'_{nl,jj'mm'} - \varepsilon_{nljm}^{(1)} \delta_{jj'} \delta_{mm'} \right] C_{nlj'm'}^{(0)} = 0, \tag{9}$$

where

$$H'_{nl,jj'mm'} = \int \psi_{nljm}^{(0)*} H' \psi_{nlj'm'} d\vec{r}. \tag{10}$$

The operators for the relativistic correction terms up to the 2nd order of α are given by

$$\hat{H}' = \hat{H}'_{\text{mass}} + \hat{H}'_{\text{SO}} + \hat{H}'_{\text{dar}}, \tag{11a}$$

where the individual terms are given by

$$\hat{H}'_{\text{mass}} = -\frac{\hat{p}^4}{8} \alpha^2, \tag{11b}$$

$$\hat{H}'_{\text{SO}} = \frac{\alpha^2}{2} \frac{1}{r} \frac{dV}{dr} \hat{l} \cdot \hat{s}, \tag{11c}$$

$$\hat{H}'_{\text{dar}} = -\frac{\alpha^2}{4} \frac{dV}{dr} \frac{\partial}{\partial r}. \tag{11d}$$

The j coupled basis $\psi_{nljm}^{(0)}$ can be written by the uncoupled basis,

$$\psi_{nljm}^{(0)} = \sum_{m_l m_s} C(lsj; m_l m_s m) \phi_{nlm_l m_s}^{(0)}, \tag{12}$$

where the coefficient $C(lsj; m_l m_s m)$ is the Clebsh-Gordan coefficient. The uncoupled basis is given by,

$$\phi_{nlm_l m_s}^{(0)} = \frac{u_{nl}^{(0)}(r)}{r} Y_{lm_l}(\Omega) \chi_{\frac{1}{2} m_s}, \tag{13}$$

where $u_{nl}^{(0)}$ is the radial wave function of zeroth order,

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V(r) \right] u_{nl}^{(0)} = \varepsilon_{nl}^{(0)} u_{nl}^{(0)}, \tag{14}$$

Y_{lm} the spherical harmoic, and $\chi_{\frac{1}{2}m_s}$ the spin wave function. Let us consider the operator $\hat{O}$ which does not depend on angles, and introduce the notation,

$$\langle u_{nl}^{(0)}|\hat{O}|u_{nl}^{(0)}\rangle = \int_0^\infty dr r^2 \left(\frac{u_{nl}^{(0)*}}{r}\right)\hat{O}\left(\frac{u_{nl}^{(0)}}{r}\right). \tag{15}$$

The matrix element of $\hat{O}$ is calculated as

$$\begin{aligned}
\int \psi_{nljm}^{(0)*}\hat{O}\psi_{nlj'm'}^{(0)}d\vec{r} &= \sum_{m_l m_s}\sum_{m_l' m_s'} C(lsj;m_l m_s m)C(lsj';m_l' m_s' m')\langle u_{nl}^{(0)}|\hat{O}|u_{nl}^{(0)}\rangle\delta_{m_l m_l'}\delta_{m_s m_s'} \\
&= \langle u_{nl}^{(0)}|\hat{O}|u_{nl}^{(0)}\rangle \sum_{m_l m_s} C(lsj;m_l m_s m)C(lsj';m_l m_s m') \\
&= \langle u_{nl}^{(0)}|\hat{O}|u_{nl}^{(0)}\rangle\delta_{jj'}\delta_{mm'}.
\end{aligned} \tag{16}$$

On the last line, the orthogonality of the Clebsh-Gordan coefficient is used. Therefore, it is found that the mass and Darwin terms are diagonal. Using Eq. (2), the mass term ΔE_{mass} is given by

$$\Delta E_{\text{mass}} = -\frac{\alpha^2}{2}\langle u_{nl}^{(0)}|[\varepsilon_{nl}^{(0)} - V(r)]^2|u_{nl}^{(0)}\rangle, \tag{17}$$

and the Darwin term ΔE_{dar},

$$\Delta E_{\text{dar}} = -\frac{\alpha^2}{4}\int_0^\infty u_{nl}^{(0)*} r \frac{dV}{dr}\frac{d}{dr}\left(\frac{u_{nl}^{(0)}}{r}\right) dr = -\frac{\alpha^2}{4}\int_0^\infty u_{nl}^{(0)*}\frac{dV}{dr}\left(-\frac{1}{r} + \frac{d}{dr}\right) u_{nl}^{(0)} dr. \tag{18}$$

It is also shown that the spin-orbit term is diagonal. Since the operator $\hat{l}$ and $\hat{s}$ commute each other,

$$\hat{j}^2 = \hat{l}^2 + 2\hat{l}\cdot\hat{s} + \hat{s}^2. \tag{19}$$

Thus we obtain,

$$\hat{H}'_{\text{SO}} = \frac{\alpha^2}{4r}(\hat{j}^2 - \hat{l}^2 - \hat{s}^2)\frac{dV}{dr}. \tag{20}$$

With the use of Eqs. (12) and (16), the matrix element is

$$\int_0^\infty \psi_{nljm}^{(0)*}\hat{H}'_{\text{SO}}\psi_{nlj'm'}^{(0)}d\vec{r} = \frac{\alpha^2}{4}[j'(j'+1) - l(l+1) - 3/4]\langle u_{nl}^{(0)}|\frac{1}{r}\frac{dV}{dr}|u_{nl}^{(0)}\rangle\delta_{jj'}\delta_{mm'}. \tag{21}$$

Therefore, the spin orbit term ΔE_{SO} is given by

$$\begin{aligned}
\Delta E_{\text{SO}} &= \frac{\alpha^2}{4}[j(j+1) - l(l+1) - 3/4]\langle u_{nl}^{(0)}|\frac{1}{r}\frac{dV}{dr}|u_{nl}^{(0)}\rangle \\
&= \begin{cases} 0 & (j = 1/2). \\ \frac{\alpha^2}{4}l\langle u_{nl}^{(0)}|\frac{1}{r}\frac{dV}{dr}|u_{nl}^{(0)}\rangle & (j = l + 1/2), \\ -\frac{\alpha^2}{4}(l+1)\langle u_{nl}^{(0)}|\frac{1}{r}\frac{dV}{dr}|u_{nl}^{(0)}\rangle & (j = l - 1/2). \end{cases}
\end{aligned} \tag{22}$$

The spin-orbit coupling and Darwin terms involve the derivative of the potential $V(r)$. It has the singularity at orgin, and the singularity is involved as the lower limit of the radial integral to calculate the matrix element. In the appendix, we avoid calculating the derivative of the potential by considering the partial integration. In doing so, we have to calculate the derivative of the wave function $u_{nl}^{(0)}$, but it is the smooth function in space. Besides, in the Generalized pseudo spectral (GPS) method, the analytical expression of the derivative of the wave function is given.

II. PHOTO IONIZATION CROSS SECTION

The cross section for the ith subshell by absorbing photon of energy ω_{in} in the dipole approximation is given by

$$\sigma_p(i, \omega_{\text{in}}) = 4\pi^2 \alpha \omega_{\text{in}} \sum_a \delta(\varepsilon_a + I_i - \omega_{\text{in}})|\langle \varphi_a|z|\varphi_i\rangle|^2. \tag{23}$$

Here the external filed is linearly polarized along the z axis. The summation runs over all the final state satisfying the dipole selection rule for linearly polarized external fields. Since the equation Eq. (25b) is diagonal with respect to j and m, using the Eq. (12), we can write down φ_i and φ_a,

$$\varphi_i = \psi_{nljm}^{(0)}, \tag{24a}$$

$$\varphi_a = \psi_{\varepsilon_a l'j'm'}^{(0)} \tag{24b}$$

where the energy of the final state ε_a is given by

$$\varepsilon_a = \varepsilon_{nl}^{(0)} + \varepsilon_{nlj}^{(1)} + \omega_{\text{in}}, \tag{25a}$$

$$\varepsilon_{nlj}^{(1)} = \Delta E_{\text{mass}} + \Delta E_{\text{dar}} + \Delta E_{\text{SO}}. \tag{25b}$$

The dipole operator does not act on the spin part of the wave function, so the azimuthal quantum number for the spin must be constant,

$$m_s' = m_s. \tag{26}$$

In what follows, VMK refers to *Quantum Theory of Angular Momentum*, by Varshalovich, Moskalev, and Khersonskii. The dipole operator is a irreducible tonsor operator of rank 1,

so we evaluate the matrix element utlizing the Wigner Eckart theorem (VMK 13.1.1. Eq. (2)),

$$\langle\varepsilon_a l'j'm'|z|nljm\rangle = \frac{C(j1j';m0m')}{\sqrt{2j'+1}}\langle\varepsilon_a l'j'||z||nlj\rangle. \tag{27}$$

The Clebsch Gordan coefficient tells us the selection rules for j and m,

$$j' = j,\ j\pm 1, \tag{28a}$$

$$m' = m. \tag{28b}$$

Since the spin-orbit coupled basis functions do not have a parity, so $j' = j$ is also allowed. The reduced matrix element is given by (VMK 13.2.1. Eq. (5))

$$\langle\varepsilon_a l'j'||z||nlj\rangle = (-1)^{j+l'+s+1}\sqrt{(2j'+1)(2j+1)}\begin{Bmatrix} l & s & j \\ j' & 1 & l' \end{Bmatrix}\langle\varepsilon_a l'||z||nl\rangle. \tag{29}$$

Substituting Eq. (29) into (36), we have

$$\langle\varepsilon_a l'j'm'|z|nljm\rangle = (-1)^{j+l'+s+1}\sqrt{2j+1}\,C(j1j';m0m)\begin{Bmatrix} l & s & j \\ j' & 1 & l' \end{Bmatrix}\langle\varepsilon_a l'||z||nl\rangle. \tag{30}$$

The Wigner Eckart theorem of the dipole operator z for uncoupled basis is written as

$$\langle\varepsilon_a l'm_l'|z|nlm_l\rangle = \frac{C(l1l';m_l0m_l')}{\sqrt{2l'+1}}\langle\varepsilon_a l'||z||nl\rangle, \tag{31}$$

so the slection rules for l and m_l are given by

$$l' = l\pm 1 \tag{32a}$$

$$m_l' = m_l. \tag{32b}$$

Summarising Eqs. (26), (28), and (32), the selection rules are given by

$$m_s' = m_s, \tag{33a}$$

$$m_l' = m_l, \tag{33b}$$

$$m' = m = m_l + m_s, \tag{33c}$$

$$l' = l\pm 1, \tag{33d}$$

$$j' = j,\ j\pm 1 \tag{33e}$$

The left hand side can be calculated analytically as (VMK 5.9.1. Eq. (4))

$$\langle\varepsilon_a l'm_l|z|nlm_l\rangle = \sqrt{\frac{2l+1}{2l'+1}}\langle\varepsilon_a l'|r|nl\rangle C(l1l';000)C(l1l';m_l0m_l). \tag{34}$$

Therefore, we obtain the reduced matrix element in Eq. (31),

$$\langle\varepsilon_a l'||z||nl\rangle = \sqrt{2l+1}C(l1l';000)\langle\varepsilon_a l'|r|nl\rangle = (-1)^{\frac{l+1-l'}{2}}\sqrt{l_>}\langle\varepsilon_a l'|r|nl\rangle, \tag{35}$$

where the symbol $l_>$ is the bigger of l and l'. Substituting Eq. (35) into Eq. (30),

$$\langle\varepsilon_a l'j'm|z|nljm\rangle = (-1)^{j+l'+s+1+\frac{l+1-l'}{2}}C(j1j';m0m')\sqrt{(2j+1)l_>}\begin{Bmatrix} l & s & j \\ j' & 1 & l' \end{Bmatrix}\langle\varepsilon_a l'|r|nl\rangle. \tag{36}$$

Using the orthogonaliy of the Clebsch Gordan coefficient (VMK 8.1.1. Eq. (8) and 8.4.4. Eq. (17)),

$$\sum_{m=-j}^{j}C^2(j1j';m0m) = \frac{2j'+1}{3}\sum_{m=-j}^{j}C^2(jj'1;m-m0) = \frac{2j'+1}{3}, \tag{37}$$

the m-averaged matrix element squared become,

$$\frac{1}{2j+1}\sum_{m=-j}^{j}|\langle\varepsilon_a l'j'm|z|nljm\rangle|^2 = \frac{l_>(2j'+1)}{3}\begin{Bmatrix} l & s & j \\ j' & 1 & l' \end{Bmatrix}^2|\langle\varepsilon_a l'|r|nl\rangle|^2. \tag{38}$$

The photo ionization cross section is obtained taking the summation for the above formula over l' and j', whose ranges are given by the selection rule, Eqs. (33),

$$\sigma_p(i,\omega_{\mathrm{in}}) = \frac{4}{3}\pi^2\alpha\omega_{\mathrm{in}}\sum_{l'=|l-1|}^{l+1}\sum_{j'=|j-1|}^{j+1}l_>(2j'+1)|\langle\varepsilon_a l'|r|nl\rangle|^2\begin{Bmatrix} l & s & j \\ j' & 1 & l' \end{Bmatrix}^2. \tag{39}$$

Using the symmetry and orthogonality of the $6j$ symbol (VMK 9.4.2. Eq. (2) and 9.8. Eq. (3))

$$\sum_{j'=|j-1|}^{j+1}(2j'+1)\begin{Bmatrix} 1 & j & j' \\ s & l' & l \end{Bmatrix}^2 = \frac{1}{2l+1}. \tag{40}$$

With the use of this, Eq. (39) is reduced to

$$\sigma_p(i,\omega_{\mathrm{in}}) = \frac{4}{3}\pi^2\alpha\omega_{\mathrm{in}}\sum_{l'=|l-1|}^{l+1}\frac{l_>}{2l+1}|\langle\varepsilon_a l'|r|nl\rangle|^2. \tag{41}$$

Let N_j be the number of electron occupying the ith subshell, then the total photo ionization cross section is given by

$$\sigma_p^{\mathrm{tot}}(i,\omega_{\mathrm{in}}) = N_j\sigma_p(i,\omega_{\mathrm{in}}) = \frac{4}{3}\pi^2\alpha\omega_{\mathrm{in}}N_j\sum_{l'=|l-1|}^{l+1}\frac{l_>}{2l+1}|\langle\varepsilon_a l'|r|nl\rangle|^2. \tag{42}$$

III. AUGER RATE

The auger rate is defined by

$$\Gamma_{i,qq'} = 2\pi \sum_a |v_{aiqq'} - v_{aiq'q}|^2 \delta(\varepsilon_a + \varepsilon_i - \varepsilon_q - \varepsilon_{q'}), \tag{43a}$$

where the notation a and i refer to the Auguer electron and the initial hole in the orbial i, and q and q' the final holes. The summation for a runs over all the possible states for the Auger electron. The quantity $v_{aiqq'}$ and $v_{aiq'q}$ represents the matrix element of the direct and exchange terms for the two body operator. The multipole expansion of the two body operator is given by

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \sum_{\mu=-k}^{k} \frac{r_<^k}{r_>^{k+1}} (-1)^\mu C_{k\mu}(\Omega_1) C_{k-\mu}(\Omega_2), \tag{44a}$$

where

$$C_{k\mu}(\Omega) = \sqrt{\frac{4\pi}{2k+1}} Y_{k\mu}(\Omega). \tag{44b}$$

The summation running over μ gives us the scalar product of the tensor operator of rank k. Introduing the scalar quantity $T_0(k)$,

$$T_0(k) = \sum_{\mu=-k}^{k} (-1)^\mu C_{k\mu}(\Omega_1) C_{k-\mu}(\Omega_2), \tag{44c}$$

the two body oeprator is written as

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} T_0(k). \tag{44d}$$

A. non relativistc case

The direct term $v_{aiqq'}$ is given by

$$v_{aiqq'} = \langle \varepsilon_a l_a m_{la} s m_{sa}; n_i l_i m_{li} s m_{si} | \frac{1}{r_{12}} | n_q l_q m_{lq} s m_{sq}; n_{q'} l_{q'} m_{lq'} s m_{sq'} \rangle. \tag{45}$$

Introducing the $LSJM$ basis, we cast the above matrix element into

$$\begin{aligned}
v_{aiqq'} &= \sum_{L'M_{L'}} \sum_{S'M_{S'}} \sum_{J'M'} \sum_{LM_L} \sum_{SM_S} \sum_{JM} \\
&\quad C(l_a l_i L'; m_{la} m_{li} M_{L'}) C(ssS'; m_{sa} m_{si} M_{S'}) C(L'S'J'; M_{L'} M_{S'} M') \\
&\quad \times C(l_q l_{q'} L; m_{lq} m_{lq'} M_L) C(ssS; m_{sq} m_{sq'} M_S) C(LSJ; M_L M_S M) \\
&\quad \times \langle l_a l_i L'S'J'M' | \frac{1}{r_{12}} | l_q l_{q'} LSJM \rangle.
\end{aligned} \tag{46}$$

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Let us define the radial integral,

$$R_k(aiqq') = \int_0^\infty dr_1 \int_0^\infty dr_2 u_{\varepsilon_a l_a}(r_1) u_{n_i l_i}(r_2) \frac{r_<^k}{r_>^{k+1}} u_{n_q l_q}(r_1) u_{n_{q'} l_{q'}}(r_2). \tag{47}$$

Substituting Eq. (C.5),

$$
\begin{aligned}
v_{aiqq'} &= \sum_{LM_L} \sum_{SM_S} \sum_{JM} C(l_a l_i L; m_{la} m_{li} M_L) C(ssS; m_{sa} m_{si} M_S) \\
&\times\ C(l_q l_{q'} L; m_{lq} m_{lq'} M_L) C(ssS; m_{sq} m_{sq'} M_S) \\
&\times\ C^2(LSJ; M_L M_S M)(-1)^{L+l_q+l_i} \sum_{k=0}^\infty R_k(aiqq') A_{kL}(aiqq') \\
&= \sum_{LM_L} \sum_{SM_S} C(l_a l_i L; m_{la} m_{li} M_L) C(ssS; m_{sa} m_{si} M_S) \\
&\times\ C(l_q l_{q'} L; m_{lq} m_{lq'} M_L) C(ssS; m_{sq} m_{sq'} M_S) \\
&\times\ (-1)^{L+l_q+l_i} \sum_{k=0}^\infty R_k(aiqq') A_{kL}(aiqq').
\end{aligned}
$$

We know that only the terms of $M' = M$ and $M_{L'} = M_L$ contribute to the summation. This tells us that we also only need to take $M_{S'} = M_S$. And the summation over J and M are carried out using the orthogonality of the Clebsch-Gordan coefficients. We further multiply the constant τ to this quantity to keep the normalization of the $LSJM$ basis function, and redefine the quantity $v_{aiqq'}$, namely,

$$
\begin{aligned}
v_{aiqq'} &= \tau \sum_{LM_L} \sum_{SM_S} C(l_a l_i L; m_{la} m_{li} M_L) C(ssS; m_{sa} m_{si} M_S) \\
&\times\ C(l_q l_{q'} L; m_{lq} m_{lq'} M_L) C(ssS; m_{sq} m_{sq'} M_S) \\
&\times\ (-1)^{L+l_q+l_i} \sum_{k=0}^\infty R_k(aiqq') A_{kL}(aiqq'),
\end{aligned}
\tag{48a}
$$

where

$$\tau = 1 \ \text{(inequivalent electrons)}, \tag{48b}$$

$$= \frac{1}{\sqrt{2}} \ \text{(equivelent electrons)}. \tag{48c}$$

Together with the exchange term,

$$v_{aiqq'} - v_{aiq'q} = r(aiqq') M_{LS}(aiqq'), \tag{49}$$

where

$$
\begin{aligned}
r(aiqq') &= \sum_{LM_L} \sum_{SM_S} C(l_a l_i L; m_{la} m_{li} M_L) C(ssS; m_{sa} m_{si} M_S) \\
&\times\ C(l_q l_{q'} L; m_{lq} m_{lq'} M_L) C(ssS; m_{sq} m_{sq'} M_S),
\end{aligned}
\tag{50a}
$$

and

$$M_{LS}(aiqq') = \tau(-1)^{L+l_q+l_i} \sum_{k=0}^{k_{\max}} \left[R_k(aiqq') A_{kL}(aiqq') + (-1)^{L+S} R_k(aiq'q) A_{kL}(aiq'q) \right].$$

(50b)

We consider the average for the quantity Eq. (49) with respect to the initial and final holes i and q, q',

$$\frac{N_i}{2(2l_i + 1)} \times N_{l_q l_{q'}} \times \sum_{m_{li} m_{lq} m_{lq'}} |v_{aiqq'} - v_{aiq'q}|^2,$$

(51)

where the constant N_i represents the number of holes in the subshell i. The first prefactor is introduced to implement the average for the initial hole i. Let N_{l_q} and $N_{l_{q'}}$ be the occupation number of the subshell q and q'. Then the second prefactor $N_{l_q l_{q'}}$ is given by

$$N_{l_q l_{q'}} = \frac{N_{l_q} N_{l'_q}}{(4l_q + 2)(4l_{q'} + 2)}, \quad \text{(inequivalent electrons)}$$

(52a)

$$= \frac{N_{l_q}(N_{l_q} - 1)}{(4l_q + 2)(4l_q + 1)}, \quad \text{(equivalent electrons)}.$$

(52b)

The second prefactor is introduced to implement the average for the final holes q and q'. The Auger rate is obtained by summing up Eq. (51) over all the possible states of the Auger electron and multiplying 2π,

$$\Gamma_{l_i, l_q l_{q'}} = \frac{\pi N_i N_{l_q l_{q'}}}{2l_i + 1} \sum_{l_a m_a} \sum_{m_{li} m_{lq} m_{lq'}} |v_{aiqq'} - v_{aiq'q}|^2.$$

The summation over m_{lx} ($x = a, i, q, q'$) can be done analytically. For given value of L and S, the same $M_{LS}(aiqq')$ appears totally $(2L + 1)(2S + 1)$ times. So, expanding the summation of the inside of the absolute square, it looks like,

$$\sum_{m_{la} m_{li} m_{lq} m_{lq'}} \left| \sum_{LM_L} \sum_{SM_S} (\cdots) \right|^2$$

$$= \sum_{m_{la} m_{li} m_{lq} m_{lq'}} \left| \underbrace{(c_1 + c_2 + \cdots)}_{(2L+1)(2S+1)} M_{LS} + \underbrace{(c_{1'} + c_{2'} + \cdots)}_{(2L'+1)(2S'+1)} M_{L'S'} + \cdots \right|^2,$$

where c_i represents the product of four Clebsch-Gordan coefficient for a certan combination of M_L and M_S. The cross terms vanish after taking the summation over m_{lx} ($x = a, i, q, q'$) using the orthogonality of the Clebsch-Gordan coefficients. Therefore, we obtain

$$\sum_{m_{la} m_{li} m_{lq} m_{lq'}} |v_{aiqq'} - v_{aiq'q}|^2 = \sum_{LS} (2L + 1)(2S + 1)|M_{LS}(aiqq')|^2.$$

(53)

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Finally, the Auger rate becomes

$$\Gamma_{l_i,l_q l_{q'}} = \frac{\pi N_i N_{qq'}}{2l_i + 1} \sum_{l_a=0}^{l_i+l_q+l_{q'}} \sum_{L=|l_q-l_{q'}|}^{l_q+l_{q'}} \sum_{S=0}^{1} (2L+1)(2S+1)|M_{LS}(aiqq')|^2. \tag{54}$$

B. relativistc case

In relativistic case, we introduce the relativistic energy corrections to all the non relativistc subshells. We write down our basis functions in jj coupling scheme,

$$|n_q l_q j_q m_q; n_{q'} l_{q'} j_{q'} m_{q'}\rangle = \sum_{JM} C(j_q j_{q'} J; m_q m_{q'} M)|j_q j_{q'} JM\rangle, \tag{55a}$$

$$|n_a l_a j_a m_a; n_i l_i j_i m_i\rangle = \sum_{J'M'} C(j_a j_i J'; m_a m_i M')|j_a j_i J'M'\rangle, \tag{55b}$$

Using the Eq. (D.10),

$$v_{aiqq'} - v_{aiq'q} = (-1)^{J+j_i+j_{q'}+l_a+l_i}[j_a j_i j_q j_{q'}]r(aiqq')M_J(aiqq'), \tag{56a}$$

where

$$r(aiqq') = \sum_{JM} C(j_a j_i J; m_a m_i M)C(j_q j_{q'} J; m_q m_{q'} M), \tag{56b}$$

$$M_J(aiqq') = \tau \sum_{k=0}^{k_{max}} \left[R_k(aiqq')B_{kJ}(aiqq') + (-1)^{-J} R_k(aiq'q)B_{kJ}(aiq'q) \right]. \tag{56c}$$

The symbol $[ab\ldots c]$ is defined in Eq. (D.2). We consider the average over the initial and final holes in the subshell i and q, q'. Let N_q be the occupation number of the subshell q, then let us define the constant $n_{j_q j_{q'}}$,

$$n_{j_q j_{q'}} = \frac{N_{j_q} N_{j_{q'}}}{(2j_q+1)(2j_{q'}+1)} \quad \text{(inequivalent electrons)}, \tag{57a}$$

$$= \frac{N_{j_q}(N_{j_q}-1)}{2j_q(2j_q+1)} \quad \text{(equivalent electrons)}. \tag{57b}$$

Then the average is calculated as

$$\frac{N_i n_{j_q j_{q'}}}{2j_i+1} \sum_{m_i m_q m_{q'}} |v_{aiqq'} - v_{aiq'q}|^2$$

$$= N_i N_{j_q j_{q'}}(2j_a+1) \sum_{m_i m_q m_{q'}} |r(aiqq')M_J(aiqq')|^2,$$

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where

$$N_{j_q j_{q'}} = N_{j_q} N_{j_{q'}} \text{ (inequivalent electrons)}, \tag{58a}$$

$$= \frac{2j_q + 1}{2j_q} N_{j_q}(N_{j_q} - 1) \text{ (equivalent electrons)}. \tag{58b}$$

The Auger rate is obtained summing up this quantity over all the possible state of the Auger electron with the prefactor 2π,

$$\Gamma_{j_i, j_q j_{q'}} = 2\pi N_i N_{j_q j_{q'}} \sum_{l_a j_a m_a} \sum_{m_i m_q m_{q'}} (2j_a + 1)|r(aiqq')M_J(aiqq')|^2. \tag{59}$$

Recalling the discussion for non relativistic case, the summation over m_x $(x = a, i, q, q')$ is reduced to

$$\sum_{m_a m_i m_q m_{q'}} |r(aiqq')M_J(aiqq')|^2$$

$$= \sum_{m_a m_i m_q m_{q'}} \left| \sum_{J=|j_q-j_{q'}|}^{j_q+j_{q'}} \sum_{M=-J}^{J} C(j_a j_i J; m_a m_i m_a M) C(j_q j_{q'} J; m_q m_{q'}) M_J(aiqq') \right|^2$$

$$= \sum_{J=|j_q-j_{q'}|}^{j_q+j_{q'}} (2J + 1) |M_J(aiqq')|^2. \tag{60}$$

Using this result, we finally obtain,

$$\Gamma_{j_i, j_q j_{q'}} = 2\pi N_i N_{j_q j_{q'}} \sum_{l_a=0}^{l_i+l_q+l_{q'}} \sum_{j_a=|l_a-\frac{1}{2}|}^{l_a+\frac{1}{2}} \sum_{J=|j_q-j_{q'}|}^{j_q+j_{q'}} (2j_a + 1)(2J + 1)|M_J(aiqq')|^2. \tag{61}$$

IV. FLUORESCENCE RATE

Let us consider the process which the initial hole in the subshell q is filled by the electron in the subshell q' with a photon emittion of momentum $\vec{k}_F$ into a solid angle $d\Omega_F$. Let $\vec{\epsilon}_{\vec{k}_F, \lambda_F}$ be the unit vector of the polarization of the photon being indexed with the quantity λ_F. The fluorescence rate is defined by

$$\Gamma_{qq'} = \frac{\alpha^3}{2\pi}(I_q - I_{q'})^3 \sum_{\lambda_F} \int d\Omega_F \left| \langle \varphi_q | \vec{\epsilon}^*_{\vec{k}_F, \lambda_F} \cdot \vec{r} | \varphi_{q'} \rangle \right|^2, \tag{62}$$

where the summation running over λ_F indicates that the emitted photon is not polarized. In the spherical basis representation, the polarization and dipole vector are represented by

$$\epsilon_{\vec{k}_F, \lambda_F,} = \sum_{i=1}^{3} \epsilon_i \vec{e}_i, \quad \text{and} \quad \vec{r} = \sum_{i=1}^{3} r_i \vec{e}_i, \tag{63a}$$

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where $\vec{e}_i$ $(i = 1, 2, 3)$ is the unit vector in spherical basis. The coefficients are given by

$$(\epsilon_0, \epsilon_{\pm 1}) = (\cos\theta_{\lambda_F}, 0) \ (\lambda_F = 0), \tag{63b}$$

$$= \left(0, \mp e^{\pm i\varphi_{\lambda_F}} \sin\theta_{\lambda_F}\right) \ (\lambda_F = \pm 1), \tag{63c}$$

and

$$r_0 = rC_{10}(\Omega), \tag{63d}$$

$$r_{\pm 1} = rC_{1\pm 1}(\Omega). \tag{63e}$$

Here the function $C_{k\mu}$ is defined in Eq. (44b). Since both the polarization and dipole vector are irreducible tensor operator of rank 1, the inner product of them is written as,

$$\vec{\epsilon}^*_{\vec{k}_F, \lambda_F} \cdot \vec{r} = \sum_{\mu=-1}^{1} (-1)^\mu \epsilon_\mu r_{-\mu} = r\cos\theta_F C_{10}(\Omega) \ (\lambda_F = 0) \tag{63f}$$

$$= \pm r e^{\pm i\varphi_F} \sin\theta_F C_{1\mp 1}(\Omega) \ (\lambda_F = \pm 1). \tag{63g}$$

Using this result,

$$\sum_{\lambda_F} \int d\Omega_F \left| \langle \varphi_q | \vec{\epsilon}^*_{\vec{k}_F, \lambda_F} \cdot \vec{r} | \varphi_{q'} \rangle \right|^2 = \frac{8\pi}{3} \sum_{\mu=-1}^{1} |\langle \varphi_q | rC_{1\mu} | \varphi_{q'} \rangle|^2. \tag{64}$$

Therefore, the rate is reduced to

$$\Gamma_{qq'} = \frac{4}{3}\alpha^3 (I_q - I_{q'})^3 \sum_{\mu=-1}^{1} |\langle \varphi_q | rC_{1\mu} | \varphi_{q'} \rangle|^2. \tag{65}$$

A. non relativistic case

For $\mu = 0, \pm 1$, the matrix elements are evaluated utilizing the Wigner-Eckart theorem,

$$\langle \varphi_q | rC_{1\mu} | \varphi_{q'} \rangle = \langle n_q l_q m_{lq} s m_{sq} | rC_{1\mu} | n_{q'} l_{q'} m_{lq'} s m_{sq'} \rangle$$

$$= \langle u^{(0)}_{n_q l_q} | r | u^{(0)}_{n_{q'} l_{q'}} \rangle \langle l_q m_{lq} s m_{sq} | C_{1\mu} | l_{q'} m_{lq'} s m_{sq'} \rangle$$

$$= \delta_{m_{sq} m_{sq'}} \langle u^{(0)}_{n_q l_q} | r | u^{(0)}_{n_{q'} l_{q'}} \rangle \frac{C(l_{q'} 1 l_q; m_{lq'} \mu m_{lq})}{\sqrt{2l_q + 1}} \langle l_q || C_1 || l_{q'} \rangle. \tag{66}$$

Hence, the selection rules are given by

$$l_q = l_{q'} \pm 1, \tag{67a}$$

$$m_{lq} = m_{lq'}, \ m_{lq'} \pm 1. \tag{67b}$$

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Substituting Eq. (66) into (64), and using

$$\langle l_q||C_1||l_{q'}\rangle = \mp\sqrt{l_>} \ (l_{q'} = l_q \pm 1), \tag{68}$$

we obtain

$$\Gamma_{qq'} = \delta_{m_{sq'}m_{sq}}\frac{4}{3}\alpha^3(I_q - I_{q'})^3 \left|\langle u^{(0)}_{n_q l_q}|r|u^{(0)}_{n_{q'} l_{q'}}\rangle\right|^2 \frac{l_>}{2l_q+1}\sum_{\mu=-1}^{1}C^2(l_{q'}1l_q; m_{l_{q'}}\mu m_{l_q}) \tag{69}$$

Averaging out this quantity for the initial and final state q' and q,

$$\frac{1}{2(2l_q+1)}\sum_{m_{l_q}m_{sq}}\frac{1}{2(2l_{q'}+1)}\sum_{m_{l_{q'}}m_{sq'}}\Gamma_{qq'}$$
$$= \frac{2}{3}\alpha^3(I_q - I_{q'})^3\frac{l_>}{2l_{q'}+1}\frac{1}{2l_q+1}\left|\langle u^{(0)}_{n_q l_q}|r|u^{(0)}_{n_{q'} l_{q'}}\rangle\right|^2. \tag{70}$$

Let $N^H_{l_q}$ and $N_{l_{q'}}$ be the number of the holes and electrons in the subshell q and q'. Multiplying these constants to the above result, we redefine the fluorescence rate,

$$\Gamma_{qq'} = \frac{2}{3}\alpha^3(I_q - I_{q'})^3\frac{l_>}{2l_{q'}+1}\frac{N^H_{l_q}N_{l_{q'}}}{2l_q+1}\left|\langle u^{(0)}_{n_q l_q}|r|u^{(0)}_{n_{q'} l_{q'}}\rangle\right|^2. \tag{71}$$

B.   relativistic case

As well as non relativistic case,

$$\begin{aligned}
\langle\varphi_q|rC_{1\mu}|\varphi_{q'}\rangle &= \langle n_q l_q j_q m_q|rC_{1\mu}|n_{q'}l_{q'}j_{q'}m_{q'}\rangle \\
&= \langle u^{(0)}_{n_q l_q}|r|u^{(0)}_{n_{q'}l_{q'}}\rangle\langle l_q j_q m_q|C_1|l_{q'}j_{q'}m_{q'}\rangle \\
&= \langle u^{(0)}_{n_q l_q}|r|u^{(0)}_{n_{q'}l_{q'}}\rangle C(j_{q'}1j_q; m_{q'}\mu m_q)\frac{\langle l_q j_q||C_1||l_{q'}j_{q'}\rangle}{\sqrt{2j_q+1}} \\
&= \langle u^{(0)}_{n_q l_q}|r|u^{(0)}_{n_{q'}l_{q'}}\rangle C(j_{q'}1j_q; m_{q'}\mu m_q) \\
&\quad \times (-1)^{j_{q'}+l_q+s+1}\sqrt{2j_{q'}+1}\begin{Bmatrix} l_{q'} & s & j_{q'} \\ j_q & 1 & l_q \end{Bmatrix}\langle l_q||C_1||l_{q'}\rangle. \tag{72}
\end{aligned}$$

Therefore, the selection rules are given by

$$j_q = j_{q'}, \ j_{q'}\pm 1, \tag{73a}$$

$$l_q = l_{q'}\pm 1, \tag{73b}$$

$$m_q = m_{q'}, \ m_{q'}\pm 1. \tag{73c}$$

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Then we obtain

$$\Gamma_{qq'} = \frac{4}{3}\alpha^3(I_q - I_{q'})^3 l_> (2j_{q'} + 1)\left|\langle u^{(0)}_{n_q l_q}|r|u^{(0)}_{n_{q'} l_{q'}}\rangle\right|^2 \begin{Bmatrix} l_{q'} & s & j_{q'} \\ j_q & 1 & l_q \end{Bmatrix}^2$$

$$\times \sum_{\mu=-1}^{1} C^2(j_{q'} 1 j_q; m_{q'} \mu m_q) \tag{74}$$

Averaging out this quantity for the initial and final state q' and q,

$$\frac{1}{2j_q + 1}\sum_{m_q}\frac{1}{2j_{q'} + 1}\sum_{m_{q'}}\Gamma_{qq'} = \frac{4}{3}\alpha^3(I_q - I_{q'})^3 l_> \begin{Bmatrix} l_{q'} & s & j_{q'} \\ j_q & 1 & l_q \end{Bmatrix}^2 \left|\langle u^{(0)}_{n_q l_q}|r|u^{(0)}_{n_{q'} l_{q'}}\rangle\right|^2. \tag{75}$$

Let $N_{j_{q'}}$ and $N^H_{j_q}$ be the number of the electrons and holes in the subshell q' and q. Multiplying these constants to the above result, we redefine fluorescence rate,

$$\Gamma_{qq'} = \frac{4}{3}\alpha^3(I_q - I_{q'})^3 l_> N_{j_{q'}} N^H_{j_q} \begin{Bmatrix} l_{q'} & s & j_{q'} \\ j_q & 1 & l_q \end{Bmatrix}^2 \left|\langle u^{(0)}_{n_q l_q}|r|u^{(0)}_{n_{q'} l_{q'}}\rangle\right|^2. \tag{76}$$

It is easy to convert this result into the one which we obtained in non relativistic case. To this end, let us switch off the relativistic energy corrections. Summing up the matrix element Eq. (74) with respect to $m_{q'}$ and m_q,

$$\sum_{m_{q'} m_q}\Gamma_{qq'} = \frac{4}{3}\alpha^3(I_q - I_{q'})^3 l_> \left|\langle u^{(0)}_{n_q l_q}|r|u^{(0)}_{n_{q'} l_{q'}}\rangle\right|^2 (2j_{q'} + 1)(2j_q + 1)\begin{Bmatrix} l_{q'} & s & j_{q'} \\ j_q & 1 & l_q \end{Bmatrix}^2.$$

We further sum up this quantity over $j_{q'}$ and j_q. Using the orthogonality of the $6j$ symbol given by Eq. (3) in the Sec. 9. 8. in VMK,

$$\sum_{j_{q'} j_q}\sum_{m_{q'} m_q}\Gamma_{qq'} = \frac{4}{3}\alpha^3(I_q - I_{q'})^3 l_> \left|\langle u^{(0)}_{n_q l_q}|r|u^{(0)}_{n_{q'} l_{q'}}\rangle\right|^2 \frac{1}{2l_q + 1}\sum_{j_q}(2j_q + 1)$$

$$= \frac{8}{3}\alpha^3(I_q - I_{q'})^3 l_> \left|\langle u^{(0)}_{n_q l_q}|r|u^{(0)}_{n_{q'} l_{q'}}\rangle\right|^2.$$

Multiplying the prefactor,

$$\frac{N^H_{l_q}}{2(2l_q + 1)}\frac{N_{l_q}}{2(2l_{q'} + 1)}$$

to the above result, we obtain the fluorescence rate in non relativistic case.

Finally, we point out that the current relativistic approach is inappropriate for heavy atoms. Let us consider the radiative transition from $2p$ to $1s$ for $1s^{-1}$ configuration. We

obtain the following quantities:

$$l_q = 0, \quad \text{and} \quad l_{q'} = 1,$$

$$l_> = \max[l_{q'}, l_q] = l_{q'} = 1.$$

The rate in non relativistic case is then reduced to

$$\Gamma_{1s2p} = \frac{4}{3}\alpha^3 (I_{1s} - I_{2p})^3 |d(2p \to 1s)|^2,$$

where

$$d(2p \to 1s) = \langle u_{1s}^{(0)} | r | u_{2p}^{(0)} \rangle.$$

In relativistic case, with the further use of

$$j_q = \frac{1}{2}, \quad \text{and} \quad j_{q'} = \frac{1}{2}, \frac{3}{2},$$

$$\left\{ \begin{array}{ccc} l_{q'} & s & j_{q'} \\ j_q & 1 & l_q \end{array} \right\}^2 = \frac{1}{(2l_{q'}+1)(2s+1)} = \frac{1}{6},$$

we obtain the partial widths,

$$\Gamma_{1s_{1/2}2p_{j_{q'}}} = \frac{2}{9}\alpha^3 (I_{1s_{1/2}} - I_{2p_{j_{q'}}})^3 N_{j_{q'}} |d(2p \to 1s)|^2.$$

The ratio relativistic to non relativistic case is given by

$$\frac{\Gamma_{1s_{1/2}2p_{1/2}} + \Gamma_{1s_{1/2}2p_{3/2}}}{\Gamma_{1s2p}} = \frac{(I_{1s_{1/2}} - I_{2p_{1/2}})^3 + 2(I_{1s_{1/2}} - I_{2p_{1/2}})^3}{3(I_{1s} - I_{2p})^3}.$$

For the case of Uuo atom of $Z = 118$, the energy of x-ray photon being emitted in non relativistic case is $I_{1s} - I_{2p} = 139666.82$ (eV). For relativistic case, $I_{1s_{1/2}} - I_{2p_{1/2}} = 164690.11$ (eV) and $I_{1s_{1/2}} - I_{2p_{3/2}} = 172637.59$ (eV). These numerical values give us the above ratio ≈ 1.81. The numerical results for the radiative widths are given by $\Gamma_{1s2p} = 8.03$ (a.u.) in non relativistic case, and $\Gamma_{1s_{1/2}2p_{1/2}} + \Gamma_{1s_{1/2}2p_{3/2}} = 4.39 + 10.1 = 14.5$ (a.u.) in relativistic case, respectively, and the ratio of them are calculated as $14.5/8.03 = 1.81$, which is consistent with the above discussions. Since the non relativistic formula somehow gives us surprisingly accurate values even for heavy atoms, the current relativistic approach fails for heavy atoms. We need to introduce the corrections for the orbital wave functions to obtain the dipole matrix element of better quality.

V. BOUND-BOUND TRANSITIONS

The exciation cross section within dipole approximation for the transition from the initial orbital i to final orbital f is given by

$$\sigma_p(i \rightarrow f, \omega_{\rm in}) = 4\pi\alpha^2\omega_{\rm in}|\langle\varphi_f|z|\varphi_i\rangle|^2\delta(\varepsilon_f - \varepsilon_i - \omega_{\rm in}). \tag{77}$$

Here the line widths of i and f are approximated to be delta function since we assume that these are much narrower than a bandwidth of pulse. For instance, the bandwidth of pulses at 5.5 keV in SACLA experiment was considered to be 1% of the photon energy i.e. ~ 50 eV. Thie photon energy opens photo ionization for $2s$ shubshell. The width of Xe $(2s^{-1})$ configuration is about 3.6 eV, which is much smaller than the band width of pulse. The dipole operator $z = r\cos\theta = rC_{10}$ is irreducible tensor operator of rank 1, so we employ the Wigner-Eckart theorem to evaluate the matrix element.

A. Non relativistic case

The Wigner-Ecckart theorem gives us

$$\begin{aligned}
\langle\varphi_f|z|\varphi_i\rangle &= \langle n'l'm_l'm_s'|z|nlm_lm_s\rangle \\
&= \langle n'l'|r|nl\rangle\delta_{m_s'm_s}\langle l'm_l'|C_{10}|lm_l\rangle \\
&= \langle n'l'|r|nl\rangle\delta_{m_s'm_s}C(l1l'; m_l0m_l')\frac{\langle l'||C_{10}||l\rangle}{\sqrt{2l'+1}} \\
&= \pm\langle n'l'|r|nl\rangle\delta_{m_s'm_s}\sqrt{\frac{l_>}{2l'+1}}C(l1l'; m_l0m_l')
\end{aligned} \tag{78}$$

Averaging out matrix element squared with respect to the magnetic and spin quantum numbers of i and f,

$$\begin{aligned}
\frac{1}{2(2l'+1)}\sum_{m_l'm_s'}\frac{1}{2(2l+1)}\sum_{m_lm_s}|\langle\varphi_f|z|\varphi_i\rangle|^2 &= \frac{l_>|\langle n'l'|r|nl\rangle|^2}{2(2l'+1)^2(2l+1)}\sum_{m_l'm_l}C^2(l1l'; m0m') \\
&= \frac{1}{3}\frac{l_>|\langle n'l'|r|nl\rangle|^2}{2(2l'+1)(2l+1)}.
\end{aligned} \tag{79}$$

Let N_l and $N_{l'}^H$ be the number of occupations and holes in the initial and final orbitals. We redefine the cross section, Eq. (77), by replacing the matrix squared to the above result, and multiplying N_l and $N_{l'}$,

$$\sigma_p(i \rightarrow f, \omega_{\rm in}) = \frac{2}{3}\pi\alpha^2 N_l N_{l'}^H \frac{l_>|\langle n'l'|r|nl\rangle|^2}{(2l'+1)(2l+1)}\delta(\varepsilon_f - \varepsilon_i - \omega_{\rm in}). \tag{80}$$

B. Relativistic case

The Wigner-Eckart theorem in relativistic case is

$$
\begin{aligned}
\langle \varphi_f | z | \varphi_i \rangle &= \langle n'l'j'm' | r C_{10} | nljm \rangle \\
&= \langle n'l' | r | nl \rangle \langle l'j'm' | C_{10} | ljm \rangle \\
&= \langle n'l' | r | nl \rangle \frac{C(j1j'; m0m')}{\sqrt{2j'+1}} \langle l'j' || C_{10} || lj \rangle \\
&= \langle n'l' | r | nl \rangle C(j1j'; m0m') \\
&\times (-1)^{j+l'+s+1} \sqrt{2j+1}
\begin{Bmatrix} l & s & j \\ j' & 1 & l' \end{Bmatrix}
\langle l' || C_{10} || l \rangle \\
&= \mp (-1)^{j+l'+s+1} \sqrt{l_>(2j+1)} \langle n'l' | r | nl \rangle C(j1j'; m0m')
\begin{Bmatrix} l & s & j \\ j' & 1 & l' \end{Bmatrix}. \quad (81)
\end{aligned}
$$

Averaging the matrix element squared with respect to m and m',

$$
\begin{aligned}
&\frac{1}{2j'+1} \sum_{m'} \frac{1}{2j+1} \sum_{m} |\langle \varphi_f | z | \varphi_i \rangle|^2 \\
&= \frac{l_>}{2j'+1} |\langle n'l' | r | nl \rangle|^2
\begin{Bmatrix} l & s & j \\ j' & 1 & l' \end{Bmatrix}^2
\sum_{m'm} C^2(j1j'; m0m') \\
&= \frac{l_>}{3} |\langle n'l' | r | nl \rangle|^2
\begin{Bmatrix} l & s & j \\ j' & 1 & l' \end{Bmatrix}^2 \quad (82)
\end{aligned}
$$

Let N_j and $N_{j'}^H$ be the number of occupations and holes in the initial and final orbitals. As well as non-relativistic case, we obtain

$$
\sigma_p(i \to f, \omega_{\text{in}}) = \frac{4}{3} \pi \alpha^2 \omega_{\text{in}} l_> N_j N_{j'}^H \langle n'l' | r | nl \rangle|^2
\begin{Bmatrix} l & s & j \\ j' & 1 & l' \end{Bmatrix}^2
\delta(\varepsilon_f + \varepsilon_i - \omega_{\text{in}}) \quad (83)
$$

C. Convolution with pulse

Assuming that a pulse has Gaussian profile in time. Then its energy distribution is given by

$$
f(E) = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(E-\omega)^2}{2\sigma^2}}. \quad (84)
$$

Convoluting the cross section with this energy profile,

$$\int_{-\infty}^{\infty} \sigma_p(i \to f, \omega_{\text{in}}) f(\varepsilon_f) d\varepsilon_f$$

$$= \frac{2}{3}\pi\alpha^2 N_l N_{l'}^H \frac{l_>|\langle n'l'|r|nl\rangle|^2}{(2l'+1)(2l+1)} \times f(\varepsilon_i) \text{ (non relativistic)}, \tag{85a}$$

$$= \frac{4}{3}\pi\alpha^2\omega_{\text{in}}l_> N_j N_{j'}^H \langle n'l'|r|nl\rangle|^2 \left\{ \begin{array}{ccc} l & s & j \\ j' & 1 & l' \end{array} \right\}^2 \times f(\varepsilon_i) \text{ (relativistic).} \tag{85b}$$

VI. SHAKE PROCESS

A. Orbital overlap

A process accompanying a change of an electric configuration of atom from C to C' can trigger sudden change of the atomic Hamiltonian. Let $i^{(C)}$ and $i^{(C')}$ be the orbital i belonging to the atomic Hamiltonian $H^{(C)}$ and $H^{(C')}$ for the configuration C and C', respectively. Since the wave function of the orbital $i^{(C)}$ is not the eigen function of $H^{(C')}$, the electrons in $i^{(C)}$ before the decay relax into the orbital $i^{(C')}$. In this relaxation process, there is a finite probability that additional elctrons are ionized. This is called shake-off branching process. The partial shake-off branching ratio γ_i for the electrons in the orbital i is given by

$$\gamma_i = N_{i^{(C')}} \left(1 - \left|\langle i^{(C')}|i^{(C)}\rangle\right|^2, \right) \tag{86a}$$

Let $\Gamma(C \to C')$ be the rate of one of decay channels which makes the transition from C to C'. Then the corresponding shake-off branching rate is

$$\gamma_i\Gamma(C \to C'). \tag{86b}$$

When an additional electron is ionized by shake-off, the kinetic energy of the electron $\varepsilon_a^{(C)}$ being ionized by the decay process from C to C' is then substracted by the binding energy of the electron in $i^{(C')}$,

$$\varepsilon_a^{(C)} - (-\varepsilon_i^{(C')}). \tag{86c}$$

If the above qunatity is negative, the electron is not ionzied by shake-off process from the orbital $i^{(C')}$. Summing up the partial shake-off branching ratio over all the orbitals, we obtain the total shake-off branching ratio γ,

$$\gamma = \sum_i \gamma_i. \tag{86d}$$

The rate which does not accompany the shake-off processes after the decay from C to C' is given by

$$(1 - \gamma)\,\Gamma(C \rightarrow C'). \tag{86e}$$

B.   Determinant overlap

N-body wave function $\Phi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N)$ is written as

$$\Phi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N) = \sqrt{N!}\hat{A}\Phi_H(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N), \tag{87}$$

where the function $\Phi_H(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N)$ is the Hartee product given by

$$\Phi_H(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N) = \phi_1(\vec{x}_1)\phi_2(\vec{x}_2)\ldots\phi_N(\vec{x}_N). \tag{88}$$

The operator A is the antisymmetrizer defined by,

$$\hat{A} = \frac{1}{N!}\sum_P (-1)^p \hat{P}, \tag{89a}$$

where $\hat{P}$ is the permutation operator. The symbol p represents the parity of a permutation. We define the parity of the Hartree Product Eq. (88) as $+1$, and the others $+1$ or -1 either the number of permutations are even or odd. The summation in Eq. (87) runs over all the possible permutations multiplied by the parity. The important properties of $\hat{A}$ are

$$\hat{A}^2\Phi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N) = \hat{A}\Phi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N). \tag{89b}$$

$$\hat{A}^\dagger = A. \tag{89c}$$

Using them, the derterminant overlap is thus given by

$$
\begin{aligned}
\langle \Phi' | \Phi \rangle &= N! \int \hat{A}^* \left[\phi'_1(\vec{x}_1) \phi'_2(\vec{x}_2) \ldots \phi'(\vec{x}_N) \right] \hat{A} \left[\phi_1(\vec{x}_1) \phi_2(\vec{x}_2) \ldots \phi(\vec{x}_N) \right] d\vec{x} \\
&= N! \int \phi'_1(\vec{x}_1) \phi'_2(\vec{x}_2) \ldots \phi'(\vec{x}_N) \hat{A}^2 \left[\phi_1(\vec{x}_1) \phi_2(\vec{x}_2) \ldots \phi(\vec{x}_N) \right] d\vec{x} \\
&= N! \int \phi'_1(\vec{x}_1) \phi'_2(\vec{x}_2) \ldots \phi'(\vec{x}_N) \hat{A} \left[\phi_1(\vec{x}_1) \phi_2(\vec{x}_2) \ldots \phi(\vec{x}_N) \right] d\vec{x} \\
&= \int \phi'_1(\vec{x}_1) \phi'_2(\vec{x}_2) \ldots \phi'(\vec{x}_N) \sum_P (-1)^p \hat{P} \left[\phi_1(\vec{x}_1) \phi_2(\vec{x}_2) \ldots \phi(\vec{x}_N) \right] d\vec{x} \\
&= \sum_{\sigma_1, \ldots, \sigma_N} (-1)^p \langle \phi'_1 | \phi_{\sigma_1} \rangle \langle \phi'_2 | \phi_{\sigma_2} \rangle \ldots \langle \phi'_N | \phi_{\sigma_N} \rangle \\
&= \det \begin{pmatrix}
\langle \phi'_1 | \phi_1 \rangle & \langle \phi'_1 | \phi_2 \rangle & \cdots & \langle \phi'_1 | \phi_N \rangle \\
\langle \phi'_2 | \phi_1 \rangle & \langle \phi'_2 | \phi_2 \rangle & \cdots & \langle \phi'_2 | \phi_N \rangle \\
\vdots & \vdots & & \vdots \\
\langle \phi'_N | \phi_1 \rangle & \langle \phi'_N | \phi_2 \rangle & \cdots & \langle \phi'_N | \phi_N \rangle
\end{pmatrix}.
\end{aligned}
\tag{90}
$$

The summation on the last line but one runs over all the possible combinations of $\sigma_1, \ldots, \sigma_N$. The determinat overlap fails in relativistic case. For instance, for the case of Ne atom, the matrix Eq. (90) is written as

$$
\langle \Phi' | \Phi \rangle = \det \begin{pmatrix}
\langle \phi'_{1s} | \phi_{1s} \rangle & \langle \phi'_{1s} | \phi_{2s} \rangle & 0 & 0 \\
\langle \phi'_{2s} | \phi_{1s} \rangle & \langle \phi'_{2s} | \phi_{2s} \rangle & 0 & 0 \\
0 & 0 & \langle \phi'_{2p_-} | \phi_{2p_-} \rangle & \langle \phi'_{2p_-} | \phi_{2p_+} \rangle \\
0 & 0 & \langle \phi'_{2p_+} | \phi_{2p_+} \rangle & \langle \phi'_{2p_+} | \phi_{2p_+} \rangle
\end{pmatrix}.
\tag{91}
$$

Since $\langle \phi'_{2p_-} | \phi_{2p_-} \rangle = \langle \phi'_{2p_-} | \phi_{2p_+} \rangle = \langle \phi'_{2p_+} | \phi_{2p_+} \rangle = \langle \phi'_{2p_+} | \phi_{2p_+} \rangle$, the rank of the matrix is 3. So, the determinant is 0.

C. Thomas model (adiabatic approximation)

The original idea is found in T. D. Thomas, PRL **52**, 417 (1984). Let $H(t)$ be the N-body time-dependent Hamiltonian as

$$
H(t) = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \frac{Z(t)}{r_i} \right) + \sum_{i \neq j} \frac{1}{r_{ij}},
\tag{92}
$$

where

$$
Z(t) = Z + q(t).
\tag{93a}
$$

The function $q(t)$ is given by the error function,

$$q(t) = \frac{1}{\sqrt{2\pi t_0}} \int_{-\infty}^{t} e^{-\frac{t'^2}{2t_0^2}} dt'. \tag{93b}$$

The important properties of $q(t)$ are

$$\lim_{t \to -\infty} = 0 \quad \text{and} \quad \lim_{t \to \infty} q(t) = 1. \tag{93c}$$

The function $q(t)$ models the photo ionization in which the nuclar charge Z at $t = -\infty$ increases to $Z + 1$ as $t = \infty$ by the leave of the photo electron of the time scale t_0 from a parent ion.

The solution of the TDSE

$$i\frac{\partial}{\partial t}|\Psi(t)\rangle = H(t)|\Psi(t)\rangle \tag{94}$$

is expanded into

$$|\Psi(t)\rangle = e^{i\chi(t)} \left[c_0(t)|\Phi_0(t)\rangle e^{-i\int_{-\infty}^{t} E_0(t')dt'} + \sum_{i,r} c_i^r(t)|\Phi_i^r(t)\rangle e^{-i\int_{-\infty}^{t} E_i^r(t')dt'} \right.$$

$$\left. + \sum_i \int_0^\infty c_i^E(t')|\Phi_i^E(t)\rangle e^{-iEt} dE \right]. \tag{95}$$

The function $|\Phi_0(t)\rangle$ represents the ground state configulation, $|\Phi_i^r\rangle$ the configurations of shake-up states, $|\Phi_i^E(t)$ those with a shake-off electron. These are the eigen function of the Hamiltonian $H(t)$,

$$H(t)|\Phi_0(t)\rangle = E_0|\Phi_0(t)\rangle, \tag{96a}$$

$$H(t)|\Phi_i^r(t)\rangle = E_i^r|\Phi_i^r(t)\rangle, \tag{96b}$$

$$H(t)|\Phi_i^E(t)\rangle = E|\Phi_i^E(t)\rangle. \tag{96c}$$

The function $|\Phi_i^E(t)\rangle$ is energy normalized,

$$\langle\Phi_i^E|\Phi_j^{E'}\rangle = \delta_{ij}\delta(E - E'). \tag{96d}$$

In the case $E = E'$ but $i \neq j$, the right hand side of the above equation vanishes. It is found that $\frac{\partial H}{\partial t} = -\sum_i \frac{q'(t)}{r_i}$ is a one-electron operator. Using the Hellman-Feynman theorem, the matrix elements with repsect to *determinants* reduce to these with respect to *orbitals*,

$$\langle\Phi_i^r(t)|\frac{\partial H}{\partial t}|\Phi_i^r(t)\rangle = \frac{dE_i^r}{dt}, \tag{97a}$$

$$\langle\Phi_0(t)|\frac{\partial}{\partial t}|\Phi_i^r(t)\rangle = \frac{\langle\Phi_0(t)|\frac{\partial H}{\partial t}|\Phi_i^r(t)\rangle}{E_i^r(t) - E_0(t)} = -\frac{\langle i(t)|\frac{1}{r}|r(t)\rangle}{E_i^r(t) - E_0(t)}q'(t), \tag{97b}$$

$$\langle\Phi_j^s(t)|\frac{\partial}{\partial t}|\Phi_i^r(t)\rangle = \frac{\langle\Phi_j^s(t)|\frac{\partial H}{\partial t}|\Phi_i^r(t)\rangle}{E_i^r(t) - E_j^s(t)} = 0 \quad (i \neq j, \quad r \neq s). \tag{97c}$$

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The algebra in the Hartree-Fock approximation is given in the chapter two in A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry.* Let $\chi(t)$ be

$$\chi(t) = i \int_{-\infty}^{t} \langle \Phi_0(t') | \frac{\partial}{\partial t'} | \Phi_0(t') \rangle dt', \tag{98}$$

the equation for the coefficients are thus given by

$$\frac{dc_0}{dt} = \sum_{i,r} \frac{\langle i(t) | \frac{1}{r} | r(t) \rangle}{E_i^r(t) - E_0(t)} q'(t) c_i^r(t) e^{-i \int_{-\infty}^{t} \left[E_i^r(t') - E_0(t') \right] dt'}$$

$$+ \sum_i \int_0^{\infty} \frac{\langle i(t) | \frac{1}{r} | E \rangle}{E - E_0(t)} q'(t) c_i^E(t) e^{-iEt + i \int_{-\infty}^{t} E_0(t') dt'} dE, \tag{99a}$$

$$i \frac{dc_j^s}{dt} = \left(\frac{d\chi}{dt} - i \frac{dE_j^s}{dt} \right) c_j^s(t) + i \frac{\langle s(t) | \frac{1}{r} | j(t) \rangle}{E_j^s(t) - E_0(t)} q'(t) c_0(t) e^{-i \int_{-\infty}^{t} \left[E_0(t') - E_j^s(t') \right] dt'}, \tag{99b}$$

$$\frac{dc_j^{E'}}{dt} = \frac{\langle E' | \frac{1}{r} | j(t) \rangle}{E_j^{E'} - E_0(t)} q'(t) c_0(t) e^{-i \int_{-\infty}^{t} E_0(t') dt' + iE't}. \tag{99c}$$

In the last equation of the above, the transitions between two differnt shake-off configurations are ignored. The initial condition of Eqs. (99) is,

$$c_0(-\infty) = 1, \text{ and } c_i^r(-\infty) = c_i^E(-\infty) = 0. \tag{100}$$

Eqs. (99) can be solved iteratively. Assuming the zeroth order solution the same as the initial condition,

$$c_0^{(0)}(t) = 1, \text{ and } c_i^{r(0)}(t) = c_i^{E(0)}(t) = 0, \tag{101}$$

the first order solution is given by

$$c_0^{(1)}(t) = 1, \tag{102a}$$

$$c_j^{s(1)}(t) = \frac{\mu_{j \to s}}{\Delta E_{j \to s,0}} e^{-\frac{\Delta E_{j \to s,0}^2}{2} t_0^2}. \tag{102b}$$

A.   SPIN-ORBIT TERM H'_{SO}

Here, we leave some technical details to evaluate the matirx element of the spin orbit and Darwin terms avoiding the Coulomb singularity.

$$I_{nl} = \langle u_{nl}^{(0)} | \frac{1}{r} \frac{dV}{dr} | u_{nl}^{(0)} \rangle = \frac{1}{r} V \left[u_{nl}^{(0)} \right]^2 \Big|_0^{\infty} - \int_0^{\infty} V(r) \frac{d}{dr} \left\{ \frac{1}{r} \left[u_{nl}^{(0)}(r) \right]^2 \right\} dr$$

$$= -A_{nl} + \int_0^{\infty} V \left\{ \frac{1}{r^2} \left[u_{nl}^{(0)} \right]^2 - \frac{2}{r} u_{nl}^{(0)} \frac{du_{nl}^{(0)}}{dr} \right\} dr, \tag{A.1}$$

where

$$A_{nl} = \lim_{r \to 0} \left\{ \frac{1}{r} V(r) \left[u_{nl}^{(0)}(r) \right]^2 \right\}. \tag{A.2}$$

Near the origin, the potential $V(r)$ becomes hydrogenic i.e. $-Z/r$. Then the wave function $u_{nl}^{(0)}$ behaves $\sim c_{nl} r^{l+1}$. Therefore,

$$
\begin{aligned}
A_{nl} &= \lim_{r \to 0} \left[\frac{1}{r} \times \left(-\frac{Z}{r} \right) \times (c_{nl} r^{l+1})^2 \right] \\
&= -\lim_{r \to 0} \left[Z c_{nl}^2 r^{2l} \right] \\
&= \begin{cases} -Z c_{ns}^2 & (l = 0), \\ 0 & (l \neq 0). \end{cases}
\end{aligned} \tag{A.3}
$$

For s state, A_{ns} has a finite value. However, the energy correction for s state due to the spin-orbit coupling is zero. So, it is found that A_{nl} does not play a role in spin-orbit coupling.

B. DARWIN TERM H_{dar}'

Using the results of the spin-orbit term Eq. (A.1),

$$
\begin{aligned}
\langle u_{nl}^{(0)} | H_{\text{dar}}' | u_{nl}^{(0)} \rangle &= \int_0^\infty \frac{u_{nl}^{(0)}}{r} \frac{dV}{dr} \frac{\partial}{\partial r} \left(\frac{u_{nl}^{(0)}}{r} \right) r^2 dr \\
&= \int_0^\infty \left(-\frac{1}{r} \frac{dV}{dr} \left[u_{nl}^{(0)} \right]^2 + \frac{dV}{dr} u_{nl}^{(0)} \frac{du_{nl}^{(0)}}{dr} \right) dr \\
&= -I_{nl} + \int_0^\infty \frac{dV}{dr} u_{nl}^{(0)} \frac{du_{nl}^{(0)}}{dr} dr \\
&= -I_{nl} + V u_{nl}^{(0)} \frac{du_{nl}^{(0)}}{dr} \bigg|_0^\infty - \int_0^\infty V \left\{ \left(\frac{du_{nl}^{(0)}}{dr} \right)^2 + u_{nl}^{(0)} \frac{d^2 u_{nl}^{(0)}}{dr^2} \right\} dr \\
&= -I_{nl} - B_{nl} - \int_0^\infty V \left\{ \left(\frac{du_{nl}^{(0)}}{dr} \right)^2 + u_{nl}^{(0)} \frac{d^2 u_{nl}^{(0)}}{dr^2} \right\} dr, \tag{B.1}
\end{aligned}
$$

where

$$
\begin{aligned}
B_{nl} &= \lim_{r \to 0} \left[V(r) u_{nl}^{(0)}(r) \frac{du_{nl}^{(0)}(r)}{dr} \right] \\
&= \lim_{r \to 0} \left[-\frac{Z}{r} \times c_{nl} r^{l+1} \times (l+1) c_{nl} r^l \right] \\
&= \lim_{r \to 0} \left[-Z(l+1) c_{nl}^2 r^{2l} \right] \\
&= \begin{cases} -Z c_{ns}^2 & (l = 0), \\ 0 & (l \neq 0). \end{cases}
\end{aligned} \tag{B.2}
$$

It is thus found that B_{nl} vanishes for nonzero l states. For s state, it has a finite value, but it cancels out A_{ns} of I_{ns}. So, the value A_{ns} and B_{ns} does not contribute to the Darwin term. So, the Darwin term becomes,

$$
\langle u_{nl}^{(0)} | H_{\mathrm{dar}}' | u_{nl}^{(0)} \rangle = \int_0^\infty V \left\{ -\frac{1}{r^2} \left[u_{nl}^{(0)} \right]^2 + \frac{2}{r} u_{nl}^{(0)} \frac{du_{nl}^{(0)}}{dr} - \left(\frac{du_{nl}^{(0)}}{dr} \right)^2 - u_{nl}^{(0)} \frac{d^2 u_{nl}^{(0)}}{dr^2} \right\} dr \tag{B.3}
$$

The 2nd derivative is further eliminated using the Schrödinger equation.

C. AUGER MATRIX ELEMENT IN $LSJM$ SCHEME

Regarding the quantity $T_0(k) = T_0(k) \cdot 1$, using the Wigner-Eckart theorem,

$$
\begin{aligned}
&\langle l_a l_i L' S' J' M' | \frac{1}{r_{12}} | l_q l_{q'} L S J M \rangle \\
&= \delta_{J'J} \delta_{M'M} (-1)^{J+L+S'} \sum_{k=0}^\infty R_k(aiqq') \begin{Bmatrix} L' & L & 0 \\ S & S' & J \end{Bmatrix} \langle L' \| T_0(k) \| L \rangle \langle S' \| 1 \| S \rangle \\
&= \delta_{J'J} \delta_{M'M} \delta_{S'S} (-1)^{J+L+S'} \sqrt{2S'+1} \sum_{k=0}^\infty R_k(aiqq') \begin{Bmatrix} L' & L & 0 \\ S & S' & J \end{Bmatrix} \langle L' \| T_0(k) \| L \rangle \\
&= \delta_{J'J} \delta_{M'M} \delta_{S'S} \delta_{L'L} (-1)^{2(J+L+S)} \sum_{k=0}^\infty R_k(aiqq') \frac{\langle L' \| T_0(k) \| L \rangle}{\sqrt{2L'+1}}.
\end{aligned} \tag{C.1}
$$

Using the Wigner-Eckart theorem,

$$
\langle L' M_{L'} | T_0(k) | L M_L \rangle = \frac{C(L'0L; M_{L'}0M_L)}{\sqrt{2L'+1}} \langle L' \| T_0(k) \| L \rangle = \frac{\delta_{L'L} \delta_{M_{L'} M_L}}{\sqrt{2L'+1}} \langle L' \| T_0(k) \| L \rangle. \tag{C.2}
$$

Regarding the quantity $T_0(k)$ as a scalar product of irreducible tensor operator of rank k, the left hand side is written also as

$$\langle L'M_{L'}|T_0(k)|LM_L\rangle = \delta_{L'L}\delta_{M_{L'}M_L}(-1)^{L+l_q+l_i} \begin{Bmatrix} l_a & l_q & k \\ l_{q'} & l_i & L \end{Bmatrix} \langle l_a||C_k||l_q\rangle\langle l_i||C_k||l_{q'}\rangle. \quad \text{(C.3)}$$

Threfore the reduced matrix element is given by

$$\frac{\langle L'M_{L'}||T_0(k)||LM_L\rangle}{\sqrt{2L'+1}} = \delta_{L'L}\delta_{M_{L'}M_L}(-1)^{L+L_q+l_i} \begin{Bmatrix} l_a & l_q & k \\ l_{q'} & l_i & L \end{Bmatrix} \langle l_a||C_k||l_q\rangle\langle l_i||C_k||l_{q'}\rangle. \quad \text{(C.4)}$$

Using this result, Eq. (C.1) reduces to

$$\langle l_a l_i L'S'J'M'|\frac{1}{r_{12}}|l_q l_{q'}LSJM\rangle = \delta_{J'J}\delta_{M'M}\delta_{S'S}\delta_{L'L}\delta_{M_{L'}M_L}$$

$$\times (-1)^{L+l_q+l_1}\sum_{k=0}^{\infty} R_k(aiqq')A_{kL}(aiqq'), \quad \text{(C.5)}$$

where

$$A_{kL} = \begin{Bmatrix} l_a & l_q & k \\ l_{q'} & l_i & L \end{Bmatrix} \langle l_a||C_k||l_q\rangle\langle l_i||C_k||l_{q'}\rangle. \quad \text{(C.6)}$$

The selection rules give us the cut-off for the summation over k. These are found in $6j$ symbol and the reduced matrix elements in the function A_{kL}. For the direct term $v_{aiqq'}$,

$$|l_q - k| \le l_a \le l_q + k, \quad \text{(C.7a)}$$

$$|l'_q - l_i| \le k \le l_{q'} + l_i, \quad \text{(C.7b)}$$

$$l_a + k + l_q = \text{even}, \quad \text{(C.7c)}$$

$$l_i + k + l_{q'} = \text{even}. \quad \text{(C.7d)}$$

Substituting the second equation into the first, we obtain

$$l_a \le l_i + l_q + l_{q'}. \quad \text{(C.8)}$$

Rewriting Eq. (C.7a),

$$|l_a - l_q| \le k \le l_a + l_q, \quad \text{(C.9)}$$

and summing to Eq. (C.7b) and using Eq. (C.8),

$$k \le \frac{1}{2}(l_i + l_q + l_{q'} + l_q) \le l_i + l_q + l_{q'} = k_{\max}. \quad \text{(C.10)}$$

Repeating this procedure for the exchange term, we obtain the same results Eqs (C.8) and (C.10).

D. AUGER MATRIX ELEMENT IN jj COUPLING SCHEME

The direct term is evaluated as (VMK 13. 2. 1 Eq. (5))

$$\langle j_a j_i J'M' | \frac{1}{r_{12}} | j_q j_{q'} JM \rangle$$

$$= \delta_{J'J} \delta_{M'M} (-1)^{J+j_q+j_i} \sum_{k=0}^{\infty} R_k(aiqq') \begin{Bmatrix} j_a & j_q & k \\ j_{q'} & j_i & J \end{Bmatrix} \langle j_a || C_k || j_q \rangle \langle j_i || C_k || j_{q'} \rangle$$

$$= \delta_{J'J} \delta_{M'M} (-1)^{J+j_q+j_i} \sum_{k=0}^{\infty} R_k(aiqq') \begin{Bmatrix} j_a & j_q & k \\ j_{q'} & j_i & J \end{Bmatrix}$$

$$\times \ (-1)^{j_q+l_a+s+k} \sqrt{(2j_a+1)(2j_q+1)} \begin{Bmatrix} l_q & s & j_q \\ j_a & k & l_a \end{Bmatrix} \langle l_a || C_k || l_q \rangle$$

$$\times \ (-1)^{j_{q'}+l_i+s+k} \sqrt{(2j_i+1)(2j_{q'}+1)} \begin{Bmatrix} l_{q'} & s & j_{q'} \\ j_i & k & l_i \end{Bmatrix} \langle l_i || C_k || l_{q'} \rangle$$

$$= \delta_{J'J} \delta_{M'M} (-1)^{J+j_i+j_{q'}+l_a+l_i} [j_a j_i j_q j_{q'}] \sum_{k=0}^{\infty} R_k(aiqq') B_{kJ}(aiqq'), \tag{D.1}$$

where

$$[ab\ldots c] = \sqrt{(2a+1)(2b+1)\ldots(2c+1)}, \tag{D.2}$$

and

$$B_{kJ}(aiqq') = \begin{Bmatrix} j_a & j_q & k \\ j_{q'} & j_i & J \end{Bmatrix} \begin{Bmatrix} l_q & s & j_q \\ j_a & k & l_a \end{Bmatrix} \begin{Bmatrix} l_{q'} & s & j_{q'} \\ j_i & k & l_i \end{Bmatrix} \langle l_a || C_k || l_q \rangle \langle l_i || C_k || l_{q'} \rangle. \tag{D.3}$$

The radial integral $R_k(aiqq')$ is defined in Eq. (47). Writing down the selectrion rules from the three $6j$ symbols and two reduced matrix elements in Eq. (D.3),

$$|j_a - j_q| \le k \le j_a + j_q, \tag{D.4a}$$

$$|j_{q'} - j_i| \le k \le j_{q'} + j_i, \tag{D.4b}$$

$$|l_q - l_a| \le k \le l_q + l_a, \tag{D.4c}$$

$$|l_{q'} - l_i| \le k \le l_{q'} + l_i, \tag{D.4d}$$

$$l_a + k + l_q = \text{even}, \tag{D.4e}$$

$$l_i + k + l_{q'} = \text{even}. \tag{D.4f}$$

Rewriting the triangle relation for Eq. (D.4a), and using Eq. (D.4b),

$$|j_q - k| \le j_a \le j_q + k \le j_q + j_{q'} + j_i. \tag{D.5}$$

Summing up Eqs. (D.4a) and (D.4b), and using Eq. (D.5)

$$k \leq \frac{1}{2}(j_a + j_q + j_{q'} + j_i) \leq j_q + j_{q'} + j_i \leq l_q + l_{q'} + l_i + \frac{3}{2} \tag{D.6}$$

Rewriting the triangle relation for Eq. (D.4c), and using Eq. (D.4d),

$$|l_q - k| \leq l_a \leq l_q + k \leq l_i + l_q + l_{q'}. \tag{D.7}$$

Summing up Eqs. (D.4c) and (D.4d), and using Eq. (D.7),

$$k \leq l_q + l_{q'} + l_i. \tag{D.8}$$

Having Eqs. (D.6) and (D.8), the upper boundary of k is

$$k_{\max} = l_q + l_{q'} + l_i. \tag{D.9}$$

Using Eqs. (D.9), the matrix element Eq. (D.1) becomes

$$\langle j_a j_i J' M' | \frac{1}{r_{12}} | j_q j_{q'} JM \rangle = \delta_{J'J} \delta_{M'M} (-1)^{J+j_i+j_{q'}+l_a+l_i} [j_a j_i j_q j_{q'}] \sum_{k=0}^{k_{\max}} R_k(aiqq') B_{kJ}(aiqq').$$

Note that writing down the selection rules for the exchange term, one finds that Eqs. (D.5), (D.7) and (D.9) can also be applied to the exchange term. We further multiply the constant τ to this quantity, which keeps the normalization of jj coupled basis, and redefine the matrix element,

$$\langle j_a j_i J' M' | \frac{1}{r_{12}} | j_q j_{q'} JM \rangle = \delta_{J'J} \delta_{M'M} \tau (-1)^{J+j_i+j_{q'}+l_a+l_i} [j_a j_i j_q j_{q'}] \sum_{k=0}^{k_{\max}} R_k(aiqq') B_{kJ}(aiqq').$$

$$\tag{D.10}$$

The constant τ is the normalization factor for anti symmetrized wave functions,

$$\tau = 1 \text{ (inequivalent electrons)}, \tag{D.11a}$$

$$= \frac{1}{\sqrt{2}} \text{ (eqivalent electrons)}. \tag{D.11b}$$

E. COMPARISON BETWEEN $LSJM$ AND jj COUPLING SCHEME

Comparing the Auger rate in $LSJM$ scheme, Eq. (54), and the one in jj coupling scheme, Eq. (61), we notice that the summation over l_a of the Auger electron is common. So, we

only consider the sum over LS in $LSJM$ scheme, and the one over J and j_a in jj copling scheme, and compare them. Let us consider the case

$$l_{q'} = 0.$$

Note that this case still contains the Coster-Kronig transitions, and the $6j$ symbol becomes very simple. In this case, using Eq. (1) in VMK in 9. 5. 1, the function A_{kL} Eq. (C.6) reduces to

$$A_{kL}(aiqq') = (-1)^{l_a+l_q+l_i} \frac{\delta_{l_q L}\delta_{kl_i}}{\sqrt{(2l_q+1)(2k+1)}} \langle l_a||C_k||l_q\rangle\langle l_i||C_k||0\rangle,$$

$$A_{kL}(aiq'q) = (-1)^{l_a+l_q+l_i} \frac{\delta_{l_a k}\delta_{l_q L}}{\sqrt{(2l_a+1)(2l_q+1)}} \langle l_a||C_k||0\rangle\langle l_i||C_k||l_q\rangle.$$

Then the function M_{LS} Eq. (50b) becomes

$$
\begin{aligned}
M_{LS}(aiqq') &= \tau(-1)^{L+l_q+l_i} \sum_{k=0}^{k_{\max}} \Big[\, R_k(aiqq')\frac{\delta_{l_q L}\delta_{kl_i}}{\sqrt{(2l_q+1)(2k+1)}} \langle l_a||C_k||l_q\rangle\langle l_i||C_k||0\rangle \\
&\quad + (-1)^{L+S} R_k(aiq'q)\frac{\delta_{l_a k}\delta_{l_q L}}{\sqrt{(2l_a+1)(2l_q+1)}} \langle l_a||C_k||0\rangle\langle l_i||C_k||l_q\rangle \Big]. \\
&= \delta_{l_q L}\frac{\tau(-1)^{L+l_q+l_i}}{\sqrt{2l_q+1}} \Big[\frac{R_{l_i}(aiqq')}{\sqrt{2l_i+1}} \langle l_a||C_{l_i}||l_q\rangle\langle l_i||C_{l_i}||0\rangle \\
&\quad + (-1)^{L+S}\frac{R_{l_a}(aiq'q)}{\sqrt{2l_a+1}} \langle l_a||C_{l_a}||0\rangle\langle l_i||C_{l_a}||l_q\rangle \Big].
\end{aligned}
\tag{E.1}
$$

Threfore,

$$
\begin{aligned}
&\sum_{LS}(2S+1)(2L+1)|M_{LS}(aiqq')|^2 \\
&= \tau^2 \sum_S (2S+1)\Big[\frac{R_{l_i}(aiqq')}{\sqrt{2l_i+1}} \langle l_a||C_{l_i}||l_q\rangle\langle l_i||C_{l_i}||0\rangle \\
&\quad + (-1)^{l_q+S}\frac{R_{l_a}(aiq'q)}{\sqrt{2l_a+1}} \langle l_a||C_{l_a}||0\rangle\langle l_i||C_{l_q}||l_q\rangle \Big]^2 \\
&= 4\tau^2 \Big[\Big(\frac{R_{l_i}(aiqq')}{\sqrt{2l_i+1}}\Big)^2 \langle l_a||C_{l_i}||l_q\rangle^2\langle l_i||C_{l_i}||0\rangle^2 \\
&\quad - (-1)^{l_q}\frac{R_{l_i}(aiqq')}{\sqrt{2l_i+1}}\frac{R_{l_a}(aiq'q)}{\sqrt{2l_a+1}} \langle l_a||C_{l_i}||l_q\rangle\langle l_i||C_{l_i}||0\rangle\langle l_a||C_{l_a}||0\rangle\langle l_i||C_{l_q}||l_q\rangle \\
&\quad + \Big(\frac{R_{l_a}(aiq'q)}{\sqrt{2l_a+1}}\Big)^2 \langle l_a||C_{l_a}||0\rangle^2\langle l_i||C_{l_q}||l_q\rangle^2 \Big].
\end{aligned}
\tag{E.2}
$$

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For jj coupling scheme, we switch off the relativistic energy corrections. As well as the case of $LSJM$ scheme, substitutinbg $l_{q'} = 0$ and $j_{q'} = 1/2$ to the function B_{kJ}, Eq. (D.3),

$$B_{kJ}(aiqq') = \delta_{kl_i} \frac{(-1)^{s+k+j_i}}{\sqrt{2(2k+1)}} \begin{Bmatrix} j_a & j_q & k \\ \frac{1}{2} & j_i & J \end{Bmatrix} \begin{Bmatrix} l_q & s & j_q \\ j_a & k & l_a \end{Bmatrix} \langle l_a||C_k||l_q\rangle \langle l_i||C_k||0\rangle,$$

$$B_{kJ}(aiq'q) = \delta_{kl_a} \frac{(-1)^{s+k+j_a}}{\sqrt{2(2k+1)}} \begin{Bmatrix} j_a & \frac{1}{2} & k \\ j_q & j_i & J \end{Bmatrix} \begin{Bmatrix} l_q & s & j_q \\ j_i & k & l_i \end{Bmatrix} \langle l_a||C_k||0\rangle \langle l_i||C_k||l_q\rangle.$$

The function $M_J(aiqq')$, Eq. (56c), is reduced to

$$M_J(aiqq') = \frac{\tau(-1)^s}{\sqrt{2}} (-1)^{l_i+j_i} \left[\frac{R_{l_i}(aiqq')}{\sqrt{2l_i+1}} \begin{Bmatrix} j_a & j_q & l_i \\ \frac{1}{2} & j_i & J \end{Bmatrix} \begin{Bmatrix} l_q & s & j_q \\ j_a & l_i & l_a \end{Bmatrix} \langle l_a||C_{l_i}||l_q\rangle \langle l_i||C_{l_i}||0\rangle \right.$$
$$\left. + (-1)^{l_a+j_a-l_i-j_i-J} \frac{R_{l_a}(aiq'q)}{\sqrt{2l_a+1}} \begin{Bmatrix} j_a & \frac{1}{2} & l_a \\ j_q & j_i & J \end{Bmatrix} \begin{Bmatrix} l_q & s & j_q \\ j_i & l_a & l_i \end{Bmatrix} \langle l_a||C_{l_a}||0\rangle \langle l_i||C_{l_a}||l_q\rangle \right].$$

Threfore, using Eqs. (3) and (4) in VMK 9. 8.

$$\sum_{Jj_a} (2J+1)(2j_a+1)|M_J(aiqq')|^2$$

$$= \frac{\tau^2}{2} \sum_{j_a} (2j_a+1) \left[\left(\frac{R_{l_i}(aiqq')}{2l_i+1} \right)^2 \begin{Bmatrix} l_q & s & j_q \\ j_a & l_i & l_a \end{Bmatrix}^2 \langle l_a||C_{l_i}||l_q\rangle^2 \langle l_i||C_{l_i}||0\rangle^2 \right.$$

$$+ 2(-1)^{j_a-j_i} \frac{R_{l_i}(aiqq')}{\sqrt{2l_i+1}} \frac{R_{l_a}(aiq'q)}{\sqrt{2l_a+1}} \begin{Bmatrix} j_a & \frac{1}{2} & l_a \\ j_i & j_q & l_i \end{Bmatrix} \begin{Bmatrix} l_q & s & j_q \\ j_a & l_i & l_a \end{Bmatrix} \begin{Bmatrix} l_q & s & j_q \\ j_i & l_a & l_i \end{Bmatrix}$$

$$\times \langle l_a||C_{l_i}||l_q\rangle \langle l_i||C_{l_i}||0\rangle \langle l_a||C_{l_a}||0\rangle \langle l_i||C_{l_a}||l_q\rangle$$

$$\left. + \left(\frac{R_{l_a}(aiq'q)}{2l_a+1} \right)^2 \begin{Bmatrix} l_q & s & j_q \\ j_i & l_a & l_i \end{Bmatrix}^2 \langle l_a||C_{l_a}||0\rangle^2 \langle l_i||C_{l_a}||l_q\rangle^2 \right]$$

$$= \frac{\tau^2}{2} \left[\left(\frac{R_{l_i}(aiqq')}{(2l_i+1)\sqrt{2l_q+1}} \right)^2 \langle l_a||C_{l_i}||l_q\rangle^2 \langle l_i||C_{l_i}||0\rangle^2 \right.$$

$$- 2(-1)^{-l_q} \frac{R_{l_i}(aiqq')}{\sqrt{2l_i+1}} \frac{R_{l_a}(aiq'q)}{\sqrt{2l_a+1}} \begin{Bmatrix} \frac{1}{2} & j_q & l_q \\ l_a & l_i & j_i \end{Bmatrix} \begin{Bmatrix} l_q & s & j_q \\ j_i & l_a & l_i \end{Bmatrix}$$

$$\times \langle l_a||C_{l_i}||l_q\rangle \langle l_i||C_{l_i}||0\rangle \langle l_a||C_{l_a}||0\rangle \langle l_i||C_{l_a}||l_q\rangle$$

$$\left. + \frac{2[R_{l_a}(aiq'q)]^2}{2l_a+1} \begin{Bmatrix} l_q & s & j_q \\ j_i & l_a & l_i \end{Bmatrix}^2 \langle l_a||C_{l_a}||0\rangle^2 \langle l_i||C_{l_a}||l_q\rangle^2 \right].$$

Now let us recover the rate in $LSJM$ scheme starting from this formula. For a given value of l_i, we have to take into account two values of $j_{i\pm} = |l_i \pm \frac{1}{2}|$. For the each value of j_i bears totally $2j_i + 1$ degeneracies. The same is also applied to j_q and $j_{q'}$. Multiplying $(2j_i + 1)(2j_q + 1)(2j_{q'} + 1)$ to the both side, and summing over j_i, j_q, and $j_{q'}$,

$$
\sum_{j_i j_q j_{q'}} (2j_i + 1)(2j_q + 1)(2j_{q'} + 1) \sum_{J j_a} (2J + 1)(2j_a + 1)|M_J(aiqq')|^2
$$

$$
= 4\tau^2 \left[\left(\frac{R_{l_i}(aiqq')}{\sqrt{2l_i + 1}} \right)^2 \langle l_a||C_{l_i}||l_q\rangle^2 \langle l_i||C_{l_i}||0\rangle^2 \right.
$$

$$
- (-1)^{-l_q} \frac{R_{l_i}(aiqq')}{\sqrt{2l_i + 1}} \frac{R_{l_a}(aiq'q)}{\sqrt{2l_a + 1}} \langle l_a||C_{l_i}||l_q\rangle \langle l_i||C_{l_i}||0\rangle \langle l_a||C_{l_a}||0\rangle \langle l_i||C_{l_a}||l_q\rangle
$$

$$
\left. + \left(\frac{R_{l_a}(aiqq')}{\sqrt{2l_a + 1}} \right)^2 \langle l_a||C_{l_a}||0\rangle^2 \langle l_i||C_{l_a}||l_q\rangle^2 \right]. \tag{E.3}
$$

We find that the Eqs. (E.2) and (E.3) are identical. The total number of the orbitals for j_i is

$$
\sum_{j_q=|l_q-\frac{1}{2}|}^{l_q+\frac{1}{2}} (2j_q + 1) = 4l_q + 2 \ (l_q \neq 0),
$$

$$
= 2 \ (l_q = 0).
$$

The total occupation number for the subshell j_q is

$$
\sum_{j_q} N_{j_q} = N_{l_q}. \tag{E.4}
$$

Introducing the quantity $N_{l_q l_{q'}}$ defined as

$$
N_{l_q l_{q'}} = \frac{\left(\sum_{j_q} N_{j_q} \right) \left(\sum_{j_{q'}} N_{j_{q'}} \right)}{\left[\sum_{j_q} (2j_q + 1) \right] \left[\sum_{j_{q'}} (2j_{q'} + 1) \right]} = \frac{N_{l_q} N_{l_{q'}}}{2(4l_q + 2)} \ \text{(inequivalent electrons)}
$$

$$
= \frac{N_{l_q}(N_{l_q} - 1)}{2} \ \text{(equivalent electrons). (E.5)}
$$

Let N_i be the number of the holes in the subshell i. Then, the prefactor for the rate is

$$
2\pi \times \frac{N_i}{\sum_{j_i} (2j_i + 1)} \times N_{l_q l_{q'}} = \frac{\pi N_i N_{l_q l_{q'}}}{2l_i + 1}. \tag{E.6}
$$

This is identical to the prefactor in $LSJM$ scheme.