Effect of screening by external charges on the atomic orbitals and photoinduced processes within the Hartree-Fock-Slater atom

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Motivation: Coherent diffraction imaging (CDI) on (X)FELs

- (X)FELs provide brilliant radiation with extremely high peak brightness in the soft or hard x-ray regime (FLASH, LCLS, etc.)
- One of the unique opportunities offered by XFELs is single-shot imaging of individual macromolecules
- CDI [1] can determine the structure of non-crystallizing biomolecules or other nanoparticles at atomic resolution
- The intense XFEL pulses ionize the molecules \( \leadsto \) screening effects
- Effect of screening on orbital energies, Auger and fluorescence rates, cross sections, etc. \( \leadsto \) ionization potential depression

- We use a modified Hartree-Fock Slater approach, implemented in the computational toolkit XATOM [2]
- Effect of charged environment on the photoinduced processes in the context of CDI experiments

1. Standard Hartree-Fock Slater (HFS) approach [1,2]

**Effective single-electron Schrödinger equation**

\[
\left[ -\frac{1}{2} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r})
\]

**Effective potential in unscreened HFS approach**

\[
V_{\text{eff}}^{\text{HFS}}(\mathbf{r}) = -\frac{Z}{r} + \int \frac{\rho(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} d^3\mathbf{r'} + V_x(\mathbf{r})
\]

**Electron density**

\[
\rho(\mathbf{r}) = \sum_i N_{\text{elec}} \psi_i^\dagger(\mathbf{r}) \psi_i(\mathbf{r})
\]

**Slater exchange potential**

\[
V_x(\mathbf{r}) = -\frac{3}{2} \left[ \frac{3}{\pi} \rho(\mathbf{r}) \right]^{1/3}
\]

2. Debye screened HFS approach \[1\]

**Effective potential in Debye screened HFS approach**

\[
V_{\text{eff}}^D(r) = -\frac{Ze^{-r/\lambda_D}}{r} + \int \frac{\rho(r')e^{-|r-r'|/\lambda_D}}{|r-r'|} \, d^3r' + V_x^D(r)
\]

**Debye-screened exchange potential \[2,3\]**

\[
V_x^D(r) = V_x(r) F(\alpha)
\]

**Correction factor by Robinson \[2\]**

\[
F(\alpha) = 1 - \frac{\alpha^2}{6} - \frac{4}{3} \alpha \tan^{-1}\left(\frac{2}{\alpha}\right) + \frac{\alpha^2}{2} \left(1 + \frac{\alpha^2}{12}\right) \ln \left|1 + \frac{4}{\alpha^2}\right|
\]

where \(\alpha = 1/(\lambda_D k_F) = \frac{\kappa_D}{k_F}\), with the Fermi momentum \(k_F\)

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3. Ion-sphere (IS) screened HFS approach [1]

Effective potential in IS screened HFS approach

\[ V^{IS}_{\text{eff}}(r) = -\frac{Z}{r} + \int \rho(r') + \bar{n}_e - \bar{Z}_i \bar{n}_ig_{ii}(r') \frac{1}{|r - r'|} \, d^3r' + V_x(r) \]

\( \bar{n}_e \) and \( \bar{n}_i \): number densities of external electrons and ions
\( \bar{Z}_i \): effective charge of ions

Radial distribution function \( g_{ii}(r) \): fit formula [2,3] for parametrization

\[ g_{ii}(r) = 1 + a \cdot e^{-b \cdot r} \sin (c \cdot r - d) \]

with fit parameters \( a, b, c, d \) in units of \( \text{Å}^{-1} \)

Pair correlation function fit [1] for carbon @ $n_i = 2.0 \text{ g/cm}^3$ [2]

\[ g_{ii}(r) = 1 + 7.0 \exp(-1.2r) \sin(5.4r - 6.1) \]

Pair correlation function fit for carbon @ $n_i = 4.4 \text{ g/cm}^3$

$$g_{ii}(r) = 1 + 1.2 \exp(-0.16r) \sin(7.2r - 8.4)$$

$$g_a(r) = 1 + 3.1 \exp(-1.22r) \sin(4.5r - 5.9)$$
Debye screened HFS method: Orbital energy shift for carbon

\[ \lambda_D = 1.72 \, a_0 \]

\[ \lambda_D = 3.14 \, a_0 \]

\[ \lambda_D = 5.0 \, a_0 \]

\[ \lambda_D = 10.0 \, a_0 \]

\( \Delta E \) (eV)

Number of bound electrons, \( Z_b \)

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IS screened HFS method: Orbital energy shift for carbon @ $n_i = 2.0 \text{ g/cm}^3$

![Graph showing orbital energy shift (ΔE) vs. number of bound electrons ($Z_b$)]
IS screened HFS method: Orbital energy shift for carbon @ $n_i = 4.4 \text{ g/cm}^3$
Carbon total photoabsorption cross sections

- Unscreened
- Debye $\lambda_D = 5 a_0$
- Debye $\lambda_D = 10 a_0$
- $2.0 \text{ g/cm}^3, Z_i = 1$
- $2.0 \text{ g/cm}^3, Z_i = 2$

Photon energy (eV)

Cross section (Mb)
Carbon photoabsorption cross sections for each subshell

- **Unscreened**
- **Debye** $\lambda_D = 5 a_0$

**Subshells:**
- 1s
- 2s
- 2p

**Photon energy (eV):**
- 0.1
- 1
- 10

**Cross section (Mb):**
- 10
- 1
- 0.1

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Atomic scattering factor for carbon

Unscreened

Debye $\lambda_D = 1.72 \ a_0$

$2.0 \ \text{g/cm}^3, \ Z_i = 2$

$C^+$ (core hole $1s^1$)

$C^{2+}$ (double core hole $1s^0$)
Summary and outlook

- Analysis focused on the parameter regime corresponding to the dynamics within XFEL irradiated samples \( \rightarrow \) coherent diffractive imaging
- We have extended the standard HFS model and its numerical implementation within the XATOM code to include screening effects:
  A in the Debye-screened model, accounting for screening by thermalized free electrons
  B in the ion-sphere model, accounting for screening by non-thermalized electrons and ions within a net-neutral system
- We have calculated orbital energy shifts, photoabsorption cross sections, atomic scattering factors and Auger and fluorescence rates for carbon atoms and ions embedded in a charged system
- Check our models with experimental data
- Combine the Debye and ion-sphere model
- Extend our study to include self-consistent adjustment of screening parameters during the system evolution