

Notes on Scattering Theory & ePolyScat for Photoionization

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1 General framework

Within scattering theory the free particle wavefunction can be expressed as a partial wave expansion in radial and angular functions:

$$\Psi(\mathbf{r}) = \sum_{lm} A_l \chi_l(r) Y_{lm}(\theta, \phi) = \sum_{lm} \psi_{lm}(\mathbf{r}) \quad (1)$$

The exact form of $\chi_l(r)$ and A_l will depend on the potential $V(r)$. For a Coulombic potential, $V(r) \propto Z_1 Z_2 / r$, where Z_1 and Z_2 are the charges on the scattering centre and scattered particle, solutions are given by (using incoming wave normalization):

$$\chi_l(r) = F_l(r) \xrightarrow{r \rightarrow \infty} \sin \left[kr - \frac{\pi l}{2} - \frac{Z_1 Z_2}{k} \ln(2kr) + \sigma_l \right] \quad (2)$$

$$A_l = \frac{2l+1}{kr} i^l e^{-i\sigma_l} \quad (3)$$

$$\sigma_l = \arg \Gamma \left[l + 1 - i \frac{Z_1 Z_2}{k} \right] \quad (4)$$

Here the solution to the radial wavefunction, $\chi_l(r)$, is given by the (regular) *Coulomb function* $F_l(r)$. This has a complicated functional form near the scattering centre, but asymptotically goes to a sinusoidal form. Both F_l and A_l contain terms involving σ_l , this is the *Coulomb phase*, and is given by equation 4. Γ is the gamma function.

While the Coulomb potential is the exact form for a point charge, more generally a scattering system may have an additional short-range contribution to the potential (one which scales as $1/r^n$, where $n > 1$), and this contribution may be non-centrally symmetric (i.e. anisotropic). However, the strength of these short-range interactions and multi-polar contributions to the potential will fall to zero much faster than the Coulombic term, and we can define a boundary, r_c , beyond which the potential is purely Coulombic. We now have a potential defined by $V'(r < r_c)$ and $V(r \geq r_c)$. We do not know the exact (analytic) form of the wavefunction in the region $r < r_c$.

However, in the Coulombic region the radial wavefunction still has an analytic form, and is now described by:

$$\chi_l(r \geq r_c) = \cos(\delta_{lm})F_l(r) + \sin(\delta_{lm})G_l(r) \quad (5)$$

$$G_l(r) \xrightarrow{r \rightarrow \infty} \cos \left[kr - \frac{\pi l}{2} - \frac{Z_1 Z_2}{k} \ln(2kr) + \sigma_l \right] \quad (6)$$

$$A_l = \frac{2l+1}{kr} i^l e^{-i(\sigma_l + \delta_{lm})} \quad (7)$$

Here $F_l(r)$ is the regular Coulomb function as before, while $G_l(r)$ is the *irregular Coulomb function*. δ_{lm} is an additional *scattering phase shift*, which arises from the non-Coulombic part of the scattering potential. This phase shift defines the mixing of the regular and irregular Coulomb functions, and this mixing also determines the asymptotic phase shift:

$$\chi_l \xrightarrow{r \rightarrow \infty} \sin \left[kr - \frac{\pi l}{2} - \frac{Z_1 Z_2}{k} \ln(2kr) + \sigma_l + \delta_{lm} \right] \quad (8)$$

Hence the scattering phase δ_{lm} describes the effect of the non-Coulombic part of the potential, $V'(r)$, and is labelled with m to show that this may affect different components of each l -wave differently in an anisotropic scattering system. Note that the short-range part of the potential may still be centrally-symmetric, in which case only $m = 0$ components will be present. Although the form of the wavefunction is not generally known for $r < r_c$ (but could be found numerically for a given $V'(r)$), the scattering phase carries all of the information on the strength of the short range potential.

Most generally, the overall phase of each partial-wave channel is denoted $\eta_{lm} = \sigma_l + \delta_{lm}$. The total phase (including angle-dependence) can be most cleanly written as, simply, $\eta_t(\mathbf{r}) = \arg(\Psi(\mathbf{r}))$, which incorporates the scattering phases η_{lm} , as well as any additional channel-dependent phase contributions (e.g. phase contributions from Y_{lm} terms etc.).

2 Photoionization

The asymptotic wavefunction defines the final state of the system, thus any experimental observations. The solution above defines the continuum wavefunction in the presence of the scattering potential. In the case of photoionization, the amplitudes of the various partial-waves in the asymptotic limit must thus be found from some overlap from the initial state. Typically we work within the dipole regime, and the light-matter coupling at an energy E can be written:

$$d(E) = \langle \Phi_f(\mathbf{r}); \Psi(\mathbf{r}) | \hat{\mu} \cdot \mathbf{E} | \Phi_i(\mathbf{r}) \rangle \quad (9)$$

Here $\Psi(\mathbf{r})$ is the continuum (photoelectron) wavefunction of eqn. 1; $\Phi_i(\mathbf{r})$ is the initial N -electron state and $\Phi_f(\mathbf{r})$ the $N - 1$ electron final state of the ionizing molecule; $\hat{\mu}$ is the dipole operator and \mathbf{E} the incident electric field.

In terms of the observable asymptotic wavefunction (or photoelectron wavepacket), which is defined as a function of energy and angle, these matrix elements will determine the overall amplitudes and phases of the continuum wavefunction prepared via photoabsorption. Hence we can write the final asymptotic wavefunction/wavepacket as:

$$\Psi(E, \theta, \phi) = \sum_{lm} d_{l,m}(E) Y_{lm}(\theta, \phi) \quad (10)$$

where $d_{l,m}(E)$ is the dipole matrix element expanded in partial-waves. Here, the dipole matrix elements include radial integration over the continuum wavefunction of eqn. 1, and incorporates the asymptotic phases η_{lm} . The final observable is the square of this wavefunction, and (for an angle-sensitive measurement) will retain phase sensitivity over the partial-wave channels:

$$I(E, \theta, \phi) = \Psi(E, \theta, \phi) \cdot \Psi^*(E, \theta, \phi) \quad (11)$$

3 ePolyScat

The dipole matrix elements are defined in ePolyScat [1, 4, 2] by, e.g., the definition of the MF-PADs as per eqns. 1-3 of ref. [5]:

$$I_{\mu_0}(\theta_{\hat{k}}, \phi_{\hat{k}}, \theta_{\hat{n}}, \phi_{\hat{n}}) = \frac{4\pi^2 E}{cg_{p_i}} \sum_{\mu_i, \mu_f} |T_{\mu_0}^{p_i \mu_i, p_f \mu_f}(\theta_{\hat{k}}, \phi_{\hat{k}}, \theta_{\hat{n}}, \phi_{\hat{n}})|^2 \quad (12)$$

$$T_{\mu_0}^{p_i \mu_i, p_f \mu_f}(\theta_{\hat{k}}, \phi_{\hat{k}}, \theta_{\hat{n}}, \phi_{\hat{n}}) = \sum_{l, m, \mu} I_{l, m, \mu}^{p_i \mu_i, p_f \mu_f}(E) Y_{lm}^*(\theta_{\hat{k}}, \phi_{\hat{k}}) D_{\mu, -\mu_0}^1(R_{\hat{n}}) \quad (13)$$

$$I_{l, m, \mu}^{p_i \mu_i, p_f \mu_f}(E) = \langle \Psi_i^{p_i, \mu_i} | \hat{d}_\mu | \Psi_f^{p_f, \mu_f} \varphi_{klm}^{(-)} \rangle \quad (14)$$

In this formalism:

- $I_{l, m, \mu}^{p_i \mu_i, p_f \mu_f}(E)$ is the radial part of the dipole matrix element, determined from the initial and final state electronic wavefunctions $\Psi_i^{p_i, \mu_i}$ and $\Psi_f^{p_f, \mu_f}$, photoelectron wavefunction $\varphi_{klm}^{(-)}$ and dipole operator \hat{d}_μ . Here the wavefunctions are indexed by irreducible representation (i.e. symmetry) by the labels p_i and p_f , with components μ_i and μ_f respectively; l, m are angular momentum components, μ is the projection of the polarization into the MF (from a value μ_0 in the LF). Each energy and irreducible representation corresponds to a calculation in ePolyScat.
- $T_{\mu_0}^{p_i \mu_i, p_f \mu_f}(\theta_{\hat{k}}, \phi_{\hat{k}}, \theta_{\hat{n}}, \phi_{\hat{n}})$ is the full matrix element (expanded in polar coordinates) in the MF, where \hat{k} denotes the direction of the photoelectron \mathbf{k} -vector, and \hat{n} the direction of the polarization vector \mathbf{n} of the ionizing light. Note that the summation over components $\{l, m, \mu\}$ is coherent, and hence phase sensitive.

- $Y_{lm}^*(\theta_{\hat{k}}, \phi_{\hat{k}})$ is a spherical harmonic.
- $D_{\mu, -\mu_0}^1(R_{\hat{n}})$ is a Wigner rotation matrix element, with a set of Euler angles $R_{\hat{n}} = (\phi_{\hat{n}}, \theta_{\hat{n}}, \chi_{\hat{n}})$, which rotates/projects the polarization into the MF .
- $I_{\mu_0}(\theta_{\hat{k}}, \phi_{\hat{k}}, \theta_{\hat{n}}, \phi_{\hat{n}})$ is the final (observable) MFPAD, for a polarization μ_0 and summed over all symmetry components of the initial and final states, μ_i and μ_f . Note that this sum can be expressed as an incoherent summation, since these components are (by definition) orthogonal.
- g_{p_i} is the degeneracy of the state p_i .

The dipole matrix element of eqn. 14 - the radial part of the dipole matrix element - effectively defines the final state amplitude and phase. Hence, is equivalent to the general form of eqn. 9, but here expanded in terms of symmetries of the light-matter system.

In practice, the initial N -electron and final $(N - 1)$ -electron wavefunctions are defined by standard computational chemistry methods (as implemented in Gaussian, Gamess, etc.). The scattering state is solved numerically by ePS via a Schwinger variational procedure [3], and the radial dipole integrals solved based on this scattering state. Numerically, an effective range for the interaction (r_{max}) is defined by the spatial grid used in the calculation; other calculation parameters may also affect the numerical results, see ref. [3]. Matrix elements $I_{l,m,\mu}^{p_i\mu_i,p_f\mu_f}(E)$ are output for further processing, e.g. for MF-PADs or calculation of Wigner delays.

References

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