The J-matrix method in multiple scattering of electrons from uracil

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The J-matrix method

SCATTERING EQUATION

Let's start with Dirac equation:

$$\left(H_0-\frac{E}{c\hbar}+\frac{V}{c\hbar}\right)\Psi(r)\equiv\begin{pmatrix}\frac{mc^2-E+V}{c\hbar} & -\frac{d}{dr}+\frac{\kappa}{r}\\ \frac{d}{dr}+\frac{\kappa}{r} & \frac{-mc^2-E+V}{c\hbar}\end{pmatrix}\Psi(r)=\begin{pmatrix}0\\0\end{pmatrix},$$

where $V=V(r)$ is the radial scattering potential, vanishing faster than the Coulomb one, E is the total energy of the projectile. Here, $\Psi = \Psi(r)$ is the relativistic wave function, satisfying the following asymptotic condition:

$$\Psi(r)\xrightarrow{r\to\infty}\sin\left(kr-\frac{\pi l}{2}\right)+\tan\delta\cos\left(kr-\frac{\pi l}{2}\right),$$

where δ is the relativistic phase shift, l is the angular momentum of the projectile, $\kappa=-l-1$ or $\kappa=l$, and $k\equiv\sqrt{(E-mc^2)(E+mc^2)}/c\hbar$.

BASIS SET

Let's choose the basis set [1]:

$$\Phi_n^+(r)\equiv\begin{pmatrix}\phi_n^l(\lambda r)\\0\end{pmatrix},$$

$$\Phi_n^-(r)\equiv\begin{pmatrix}0\\\psi_n^l(\lambda r)\end{pmatrix},\qquad \psi_n^l(\lambda r)=\left(\frac{\kappa}{r}+\frac{d}{dr}\right)\phi_n^l(\lambda r).$$

The most popular choice of basis set ϕ_n^l is the complete oscillatory basis set:
$\phi_n^l=r(-1)^n\sqrt{\frac{2n!}{b\Gamma(n+l+3/2)}}\left(\frac{r}{b}\right)^l\exp\left(-\frac{r^2}{2b^2}\right)L_n^{(l+1/2)}\left(\frac{r^2}{b^2}\right)$.
Here, $L_n^{(\alpha)}(x)$ are the Laguerre polynomials and b is the oscillator length.
The other popular basis set is the Laguerre basis: $\phi_n^l = (\lambda r)^{l+1}\exp\left(-\frac{\lambda r}{2}\right)L_n^{(2l+1)}(\lambda r)$. In this case, functions ϕ_n^l are biorthonormal, so that $\left\langle\overline{\phi}_m^l\middle|\phi_n^l\right\rangle\equiv\int_0^\infty\overline{\phi}_m^l(\lambda r)\,\phi_n^l(\lambda r)\,dr=\delta_{mn}$, and λ is the scaling parameter.

JACOBI MATRIX

In such defined bases, the term

$$J_{mn}^{ss'}\equiv\left\langle\Phi_m^s\middle|\left(H_0-\frac{E}{c\hbar}\right)\Phi_n^{s'}\right\rangle,\quad s,s'=\pm,\quad m,\ n=0,1,\ldots$$

gives the tridiagonal form (Jacobi matrix).
These so called J-matrix elements $J_{mn}^{ss'}$ can be written as

$$J_{mn}=\begin{pmatrix}-k\epsilon\left\langle\phi_m^l\middle|\phi_n^l\right\rangle & \left\langle\psi_m^l\middle|\psi_n^l\right\rangle\\ \left\langle\psi_m^l\middle|\psi_n^l\right\rangle & -\frac{k}{\epsilon}\left\langle\psi_m^l\middle|\psi_n^l\right\rangle\end{pmatrix}_{ss'},$$

where $\epsilon\equiv\sqrt{\frac{E-mc^2}{E+mc^2}}$. Now, the J-matrix elements can be easily calculated.

SINE- AND COSINELIKE EXPANSIONS

To assure proper asymptotic behavior, we introduce sine- and cosine-like solutions of equation:

$$\left(H_0-\frac{E}{c\hbar}\right)\Psi_U=\begin{pmatrix}\Omega_U\overline{\phi}_0^l\\0\end{pmatrix},\quad \Omega_S=0,\quad \Omega_C=-\frac{\epsilon}{s_0^l}.$$

In the above, the indexes U,C corresponds to sine- and cosine-like solutions. The solutions, expanded in the selected basis, are as follows:

$$U(k,r)=\sum_{n=0}^{\infty}u_n^l(k)\begin{pmatrix}\phi_n^l\\\frac{k}{\epsilon}\psi_n^l\end{pmatrix},\quad U=S,C,\quad u=s,c.$$

Now, the following recursive relations are fulfilled:
$\sum_{n=0}^{\infty}J_{mn}s_n^l=0$, $\sum_{n=0}^{\infty}J_{mn}c_n^l=-\frac{k}{2s_0^l}\overline{\phi}_0^l$, $J_{00}s_0^l+J_{01}s_1^l=0$, $J_{00}c_0^l+J_{01}c_1^l=-\frac{k}{2s_0^l}$, $J_{n,n-1}u_{n-1}^l+J_{n,n}u_n^l+J_{n,n+1}u_{n+1}^l=0; u=s,c; n>1$

POTENTIAL SCATTERING

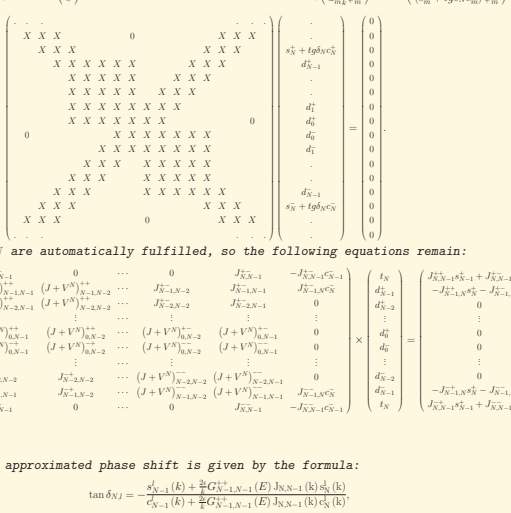
Let us replace this scattering potential by a truncated potential operator:

$$V_{mn}^N=\begin{pmatrix}\left\langle\phi_m^l\middle|V/c\hbar\phi_n^l\right\rangle & 0\\ 0 & \left\langle\psi_m^l\middle|V/c\hbar\psi_n^l\right\rangle\end{pmatrix},m,n=0,1,\ldots N-1$$

Hence, the scattering equation has the following form:

$$\left(H_0-\frac{E}{c\hbar}+V^N\right)\Psi^N(r)\equiv\begin{pmatrix}0\\0\end{pmatrix},\ \text{with expanded solution: }\Psi^N=\sum_{m=0}^{N-1}\begin{pmatrix}d_m^+\phi_m^l\\d_m^-\frac{k}{\epsilon}\psi_m^l\end{pmatrix}+\sum_{m=N}^{\infty}\begin{pmatrix}(s_m^++tg\delta_N c_m^+)\,\phi_m^l\\(s_m^-+tg\delta_N c_m^-)\,\psi_m^l\end{pmatrix}.$$

In graphical form:



Equations for $m>N$ are automatically fulfilled, so the following equations remain:

$$\begin{pmatrix}-J_{\bar{N}\bar{N}-1}^{+-}c_{\bar{N}-1}^{+} & J_{\bar{N}\bar{N}-1}^{++} & 0 & \cdots & 0 & J_{\bar{N}N-1}^{+-} & -J_{\bar{N}\bar{N}-1}^{+-}c_{\bar{N}-1}^{+}\\ J_{\bar{N}-1\bar{N}}^{+-}c_{\bar{N}}^{+} & (J+V^N)_{\bar{N}-1\bar{N}-1}^{++} & (J+V^N)_{\bar{N}-1\bar{N}-2}^{++} & \cdots & J_{\bar{N}-1\bar{N}-2}^{+-} & J_{\bar{N}-1\bar{N}-1}^{+-} & J_{\bar{N}-1\bar{N}}^{+-}c_{\bar{N}}^{+}\\ 0 & (J+V^N)_{\bar{N}-2\bar{N}-1}^{++} & (J+V^N)_{\bar{N}-2\bar{N}-2}^{++} & \cdots & J_{\bar{N}-2\bar{N}-2}^{+-} & J_{\bar{N}-2\bar{N}-1}^{+-} & 0\\ \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots\\ 0 & (J+V^N)_{0\bar{N}-1}^{++} & (J+V^N)_{0\bar{N}-2}^{++} & \cdots & (J+V^N)_{0\bar{N}-2}^{+-} & (J+V^N)_{0\bar{N}-1}^{+-} & 0\\ 0 & (J+V^N)_{0\bar{N}-1}^{-+} & (J+V^N)_{0\bar{N}-2}^{-+} & \cdots & (J+V^N)_{0\bar{N}-2}^{--} & (J+V^N)_{0\bar{N}-1}^{--} & 0\\ \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots\\ 0 & J_{\bar{N}-2\bar{N}-2}^{-+} & J_{\bar{N}-2\bar{N}-2}^{--} & \cdots & (J+V^N)_{\bar{N}-2\bar{N}-2}^{--} & (J+V^N)_{\bar{N}-2\bar{N}-1}^{--} & 0\\ J_{\bar{N}-1\bar{N}}^{-+}c_{\bar{N}}^{+} & J_{\bar{N}-1\bar{N}-1}^{-+} & J_{\bar{N}-1\bar{N}-2}^{--} & \cdots & (J+V^N)_{\bar{N}-1\bar{N}-2}^{--} & (J+V^N)_{\bar{N}-1\bar{N}-1}^{--} & J_{\bar{N}-1\bar{N}}^{--}c_{\bar{N}}^{+}\\ -J_{\bar{N}\bar{N}-1}^{-+}c_{\bar{N}-1}^{+} & J_{\bar{N}\bar{N}-1}^{-+} & 0 & \cdots & 0 & J_{\bar{N}N-1}^{--} & -J_{\bar{N}\bar{N}-1}^{--}c_{\bar{N}-1}^{+}\end{pmatrix}\times\begin{pmatrix}t_N\\d_{\bar{N}-1}^{+}\\d_{\bar{N}-2}^{+}\\\vdots\\d_0^{+}\\d_0^{-}\\\vdots\\d_{\bar{N}-2}^{-}\\d_{\bar{N}-1}^{-}\\t_N\end{pmatrix}=\begin{pmatrix}J_{\bar{N}\bar{N}-1}^{+-}s_{\bar{N}-1}^{+}+J_{\bar{N}\bar{N}-1}^{++}s_{\bar{N}-1}^{+}\\-J_{\bar{N}-1\bar{N}}^{+-}s_{\bar{N}}^{+}-J_{\bar{N}-1\bar{N}}^{++}s_{\bar{N}}^{+}\\0\\\vdots\\0\\0\\\vdots\\0\\-J_{\bar{N}-1\bar{N}}^{-+}s_{\bar{N}}^{+}-J_{\bar{N}-1\bar{N}}^{--}s_{\bar{N}}^{+}\\J_{\bar{N}\bar{N}-1}^{-+}s_{\bar{N}-1}^{+}+J_{\bar{N}\bar{N}-1}^{--}s_{\bar{N}-1}^{+}\end{pmatrix}.$$

THE SOLUTION

The tangent to the approximated phase shift is given by the formula:

$$\tan\delta_{Nl}=-\frac{s_{N-1}^l(k)+\frac{2\epsilon}{k}G_{N-1,N-1}^{++}(E)\,J_{N,N-1}(k)\,s_N^l(k)}{c_{N-1}^l(k)+\frac{2\epsilon}{k}G_{N-1,N-1}^{++}(E)\,J_{N,N-1}(k)\,c_N^l(k)},$$

where $G_{mn}^{ss'}(E) = \sum_{p=\pm}\sum_{l=0}^{N-1}c\hbar\frac{U_m^{lp}U_n^{lp}}{E_l^p-E}$, and $\left(\Gamma^l P_N^l\left(H_0+\frac{V}{c\hbar}-\frac{E}{c\hbar}\right)P_N\Gamma^l\right)_{mn}^{ss'} = \frac{1}{c\hbar}(E_n^s-E)\delta_{mn}\delta_{ss'}$. The elements s_n^l and c_n^l can be found using recursive relations mentioned above [2, 3]. Matrix G can be viewed as the matrix approximating the Green function. We expect, that $\tan\delta_{Nl}\xrightarrow{N\to\infty}\tan\delta_l$.

Differential σ_d, total σ_t, spin polarization σ_{sp} and momentum transfer σ_{mt} cross sections:

$$\sigma_d(\vartheta)=|f(\vartheta)|^2+|g(\vartheta)|^2,\quad f(\vartheta)=\frac{1}{2ik}\sum_l\{(l+1)[\exp(2i\delta_{Nl}^+)-1]+l[\exp(2i\delta_{Nl}^-)-1]\}P_l(\cos\vartheta),\quad g(\vartheta)=\frac{1}{2ik}\sum_l[\exp(2i\delta_{Nl}^+)-\exp(2i\delta_{Nl}^-)]P_l^1(\cos\vartheta),$$

$$\sigma_t(E)=\frac{4\pi}{k^2}\sum_l[(l+1)\sin^2\delta_{Nl}^+ + l\sin^2\delta_{Nl}^-],\quad \sigma_{sp}(\vartheta)=\frac{i(f(\vartheta)g^*(\vartheta)-f^*(\vartheta)g(\vartheta))}{\sigma_d(\vartheta)},\quad \sigma_{mt}(E)=\frac{4\pi}{k^2}\sum_l\frac{(l+1)(l+2)}{2l+3}\sin^2(\delta_{Nl}^+-\delta_{N,l+1}^+)+(\ldots)],$$

where δ_{Nl}^- corresponds to the solution for $\kappa=l$, and δ_{Nl}^+ for $\kappa=-l-1$.

Example: scattering from uracil

COMPUTATIONAL MODEL

We applied the method of the non-overlapped potentials (NP) as our computational model. It is based on division of a molecule area into regions - atomic spheres, which surround each atom. We assume that these spheres touch, but do not overlap [4]. Inside each of the atomic spheres, exact potential is replaced by a spherical averaged. Outside the spheres, we replace the potential by a zero potential. Such a approximation gives a model for calculating scattering phases [5].
Let's write the partial wave $\Psi(\mathbf{r})$ as the linear combination

$$\Psi(\mathbf{r})=\sum_{i=1}^{N}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}x_{ilm}\Phi_{ilm}(\mathbf{r}-\mathbf{a}_i)$$

of the atomic waves $\Phi_{ilm}(\mathbf{r})$

$$\Phi_{ilm}(\mathbf{r})=i^l\psi_{ilm}(r)Y_{lm}(\hat{\mathbf{r}}),$$

where i,l,m - atom number and angular momentum quantum numbers; ψ_{ilm} - radial wave functions; $Y_{lm}(\hat{\mathbf{r}})$ - spherical harmonics; $\mathbf{a}_i$ - points of expansion for each atom; k - radial wave number; N - number of atoms in the molecule. The coefficient x_{ilm} controls the contribution of the wave Φ_{ilm} to the partial wave.
We expand the partial wave at the vicinity of the point $\mathbf{a}_i$ in the form

$$\Psi(\mathbf{r}_i)=\sum_{lm}x_{ilm}i^l\left(\psi_{ilm}(r)+w_{ilm}j_l(kr)\right)Y_{lm}(\hat{\mathbf{r}}),$$

where $\mathbf{r}_i=\mathbf{r}+\mathbf{a}_i$. After substituting the above result to the Schrödinger equation, we obtain inhomogeneous Schrödinger equation for the function ψ_{ilm} [4]:

$$\left(H-\tfrac{1}{2}k^2\right)\psi_{ilm}(r)=-w_{ilm}V_i(r)j_l(kr),$$

where the coefficients w_{ilm} describe the contribution from waves that come from the other NPs. Hamiltonian is given by the equation

$$H=-\frac{1}{2}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{l(l+1)}{r^2}\right)+V_i(r).$$

Now, the following relation

$$w_{ilm}=\sin\delta_l(\cot\delta_{il}-\cot\delta_l),$$

is satisfied [6], which links partial phase shifts δ_{il}, coefficients w_{ilm}, and molecular partial phase shifts δ.

NUMERICAL PROCEDURE

First, the effective radii has been chosen according to [4].
Averaged static interaction over angles leads to the the following form of radial NPs [4]:

$$V_{el}(r)=-\frac{q(r)}{r},\quad r\leqslant d$$

where $q(r)$ denote effective charges, and d is the effective radius.
Nonlocal exchange interaction is described by the following effective potential [4], [7]:

$$V_{ex}(r)=-\frac{2}{\pi}k_F(r)\left(\frac{1}{2}+\frac{1-\eta^2}{4\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|\right),$$

where $k_F(r) = [3\pi^2\rho(r)]^{1/3}$ is the Fermi momentum, $\rho(r)$ denotes averaged (over angles around the atom) electron density. These densities can be obtained in ab initio calculation via density matrix and has been taken from [4]. The parameter η is given by

$$\eta=[k^2+2I+k_F^2(r)]^{1/2}/k_F(r),$$

where I - molecule ionization energy ($I=8.35$ eV in the uracil case).
The next step was to calculate phase shifts using the J-matrix method for selected electron energies, for $l=0,1$ and every atom. Then, the integral cross sections have been calculated. The procedure was repeated for two different symmetries of the molecule (denoted as A' and A).

RESULTS

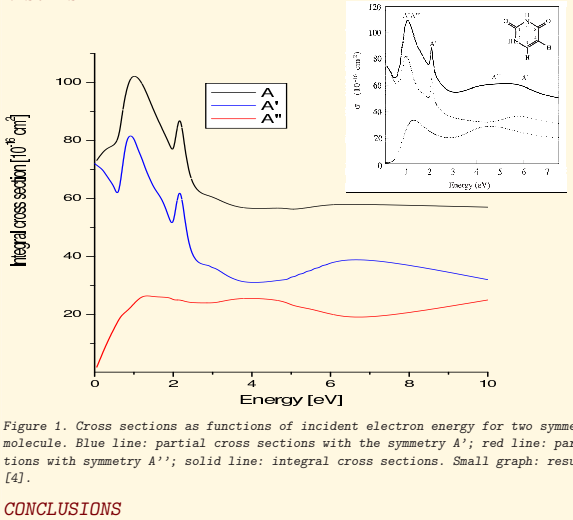


Figure 1. Cross sections as functions of incident electron energy for two symmetries of uracil molecule. Blue line: partial cross sections with the symmetry A'; red line: partial cross sections with symmetry A''; solid line: integral cross sections. Small graph: results obtained in [4].

CONCLUSIONS

We applied a simple computational model to illustrate the application of the J-matrix to scattering problems. As the results are very promising, the next step will be to extend the calculations to the relativistic case.

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