R-matrix theory for spherically symmetric potential scattering

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Motivation for the R-matrix theory

R-matrix theory for potential scattering

S-matrix and other results

Practical application – Green’s function

Conclusions
Main ideas of the R-matrix theory

- Target
Main ideas of the R-matrix theory
Main ideas of the R-matrix theory

- In the external region the electron exchange and correlation between the $N$-electron target and the scattered electron can be neglected.

- The whole interaction can be approximated by an effective single particle potential.

- Solution can be obtained using a standard methods for solving coupled differential equations.
Main ideas of the R-matrix theory

- In the internal region the electron exchange and correlation have to be taken into account.

- The $N + 1$-electron target behaves like a bound state.

- Methods analogous to that used in a bound state calculations such as configuration interaction (CI) can be adopted.
Main ideas of the R-matrix theory

- In the internal region the electron exchange and correlation have to be taken into account.
- The $N+1$-electron target behaves like a bound state.
- Methods analogous to that used in a bound state calculations such as configuration interaction (CI) can be adopted.
- Connection of the solution in the internal and external region is provided by the R-matrix, which is obtained via diagonalization of the $N+1$ Hamiltonian within the internal region.
Spherically symmetric potential scattering

Radial equation

\[ -\frac{1}{2} \frac{d\psi_l(k, r)}{dr} + \left( V(r) + \frac{l(l+1)}{2r^2} \right) \psi_l(k, r) = \epsilon \psi_l(k, r) \]

Asymptotic form of the solution

\[ \psi_l^{(+)}(k, r) \propto e^{-ikr} - e^{-i\pi l} S_l(\epsilon) e^{ikr}, \quad \epsilon = \frac{k^2}{2} \]

\[ S_l(\epsilon) = e^{2i\delta_l(\epsilon)} \]
Partitioning of the configuration space is arbitrary.

Possible choice – interaction potential vanish for \( r > r_\Omega \) and only centrifugal term appears in the radial equation.

Solution in the external region can be written in terms of Hankel functions

\[
\psi_i^{(+)}(k, r) = \sqrt{\frac{2k}{\pi}} r \left( h^{(-)}(kr) - S_i(\epsilon) h^{(+)}(kr) \right) \quad r > r_\Omega.
\]

\( S_i(\epsilon) \) is determined by the boundary condition at \( r_\Omega \).
R-matrix theory for potential scattering

- **Internal region** – discretization of the scattering continuum via diagonalization of the modified Hamiltonian

\[ H^\Omega = T + V_{\text{eff}} + L_b \]

- **Bloch operator** cancels the surface term in the kinetic energy matrix element \((\zeta_i(0) = 0)\)

\[
\langle \zeta_i | T | \zeta_j \rangle = \frac{1}{2} \int_0^{r_{\Omega}} \frac{d\zeta_i^*(r)}{dr} \frac{d\zeta_j(r)}{dr} dr - \frac{1}{2} \zeta_i^*(r_{\Omega}) \left. \frac{d\zeta_j(r)}{dr} \right|_{r=r_{\Omega}}
\]
**R-matrix basis**

- R-matrix basis

\[(T + V_{\text{eff}} + L_b) \phi_i^\Omega = E_i^\Omega \phi_i^\Omega\]

- General form of the Bloch operator

\[L_b = \frac{1}{2} \delta(r - r_\Omega) \left( \frac{d}{dr} - b \right)\]

- Properties of the R-matrix levels:

\[(T + V_{\text{eff}}) \phi_i^\Omega = E_i^\Omega \phi_i^\Omega \quad \text{for} \quad r < r_\Omega\]

\[\phi_i^\Omega (0) = 0\]

\[\langle \varphi | L_b | \phi_i^\Omega \rangle = 0 \quad \forall \ |\varphi\rangle \quad \Rightarrow \quad \frac{d}{dr} \ln (\phi_i^\Omega (r)) \bigg|_{r=r_\Omega} = b\]

- Standard choice is \( b = 0 \).
Expansion of the inner solution

- Insert the expansion $\psi_l(k, r) = \sum_j c_j \phi_j^\Omega(r)$ into the modified Schrödinger equation

$$(T + V_{\text{eff}} + L - \epsilon) \psi_l(k, r) = \sum_j c_j (E_j^\Omega - \epsilon) \phi_j^\Omega(r) = L \psi_l(k, r)$$

- Multiply by $\phi_i^{\Omega*}(r)$ and integrate, divide by $(E_i^\Omega - \epsilon)$

$$c_i = \frac{1}{2 \left( E_i^\Omega - \epsilon \right)} \phi_i^{\Omega*}(r_\Omega) \frac{d}{dr} \psi_l(k, r) \bigg|_{r=r_\Omega}$$

- Multiply by $\phi_i^\Omega(r_\Omega)$ and sum over $i$ to obtain

$$\psi_l(k, r) = \frac{1}{2} \sum_i \left| \phi_i^\Omega(r_\Omega) \right|^2 \frac{d}{dr} \psi_l(k, r) \bigg|_{r=r_\Omega}$$
Expansion of the inner solution

- Insert the expansion $\psi_l(k, r) = \sum_j c_j \phi_j^\Omega(r)$ into the modified Schrödinger equation

$$(T + V_{eff} + L - \epsilon) \psi_l(k, r) = \sum_j c_j \left( E_j^\Omega - \epsilon \right) \phi_j^\Omega(r) = L \psi_l(k, r)$$

- Multiply by $\phi_i^{\Omega*}(r)$ and integrate, divide by $(E_i^\Omega - \epsilon)$

$$c_i = \frac{1}{2 \left( E_i^\Omega - \epsilon \right)} \phi_i^{\Omega*}(r_{\Omega}) \left. \frac{d}{dr} \psi_l(k, r) \right|_{r=r_{\Omega}}$$

- Multiply by $\phi_i^\Omega(r_{\Omega})$ and sum over $i$ to obtain

$$\psi_l(k, r) = \sum_i \left| \phi_i^\Omega(r_{\Omega}) \right|^2 \frac{1}{2} \frac{1}{E_i^\Omega - \epsilon} \left. \frac{d}{dr} \psi_l(k, r) \right|_{r=r_{\Omega}}$$

$$\underbrace{R_{-matrix \; R_l(\epsilon)}}$$
In case of spherically symmetric potential scattering, \( R \)-matrix has the simple meaning of inverse logarithmic derivative of the radial component of the wave function.

\( R \)-matrix is a meromorphic function with poles on the real axis.

The \( S \)-matrix can be extracted from the external solution at the boundary of the \( R \)-matrix sphere:

\[
S_l(\epsilon) = \frac{kr\Omega h^-(kr\Omega) - R_l(\epsilon) \frac{d}{dr} \left[ krh^-(kr) \right]}{kr\Omega h^+(kr\Omega) - R_l(\epsilon) \frac{d}{dr} \left[ krh^+(kr) \right]} \bigg|_{r=r\Omega}
\]

Asymptotic case: \( r\Omega \to \infty \)

\[
S_l(\epsilon) = e^{i\pi(l+1)}e^{-2ikr\Omega} \frac{1 + ikR_l(\epsilon)}{1 - ikR_l(\epsilon)}
\]

Physically relevant poles: \( 1 - ikR_l(\epsilon) = 0 \)
Internal solution

- Expansion into the R-matrix basis

$$\Psi_l(k, r) = \sum_j c_j \phi_j^\Omega(r)$$

$$c_j = \frac{1}{2 \left( E_j^\Omega - \epsilon \right)} \phi_j^\Omega*(r_{\Omega}) \frac{d}{dr} \psi_l(k, r) \bigg|_{r=r_{\Omega}}$$

- The derivative $\frac{d}{dr} \psi_l(k, r) \bigg|_{r=r_{\Omega}}$ can be obtained from the R-matrix and normalization of the external solution:

$$\frac{d}{dr} \psi_l^{(+)}(k, r) \bigg|_{r=r_{\Omega}} = \sqrt{\frac{2k^3}{\pi r_{\Omega}^2}} h^(-)(kr) \frac{d}{dr} h^{(+)}(kr) - h^{(+)}(kr) \frac{d}{dr} h^(-)(kr)$$

$$R_l(\epsilon) \frac{d}{dr} \left[ kr h^{(+)}(kr) \right] - kr h^{(1)}(kr) \bigg|_{r=r_{\Omega}}$$
Green’s function in the R-matrix theory

- Inhomogeneous Schrödinger equation

\[(T + V_{\text{eff}} - \epsilon) \Psi(r) = \chi(r)\]

- Boundary conditions

\[\Psi(0) = 0 \quad \text{and} \quad \left. \frac{d \ln \Psi(r)}{dr} \right|_{r=r_\Omega} = A\]

- Form of the solution:

\[\Psi(r) = \int_0^{r_\Omega} G(\epsilon, r, r') \chi(r) dr\]

- \(G(\epsilon, r, r')\) is the Green’s function, which can be obtained directly by taking \(\chi(r) = \delta(r - r')\)
Derivation of the Green’s function

- Introduce Bloch operator

\[ (T + V_{\text{eff}} + L - \epsilon) \Psi(r) = \chi(r) + L \Psi(r) \]

- Expand solution into the R-matrix basis: \( \Psi(r) = \sum_j c_j \phi_j^\Omega(r) \)

\[ c_j = \frac{1}{E_j^\Omega - \epsilon} \left[ \chi_j + \frac{1}{2} \phi_j^\Omega(r)^\Omega \frac{d}{dr} \Psi(r) \bigg|_{r=r^\Omega} \right] \]

\[ \chi_j = \int_0^{r^\Omega} \phi_j^\Omega(r) \chi(r) dr \]

- The derivative is determined from the boundary condition at \( r^\Omega \)

\[ \frac{d}{dr} \Psi(r) \bigg|_{r=r^\Omega} = \frac{A}{1 - AR_l(\epsilon)} \sum_i \frac{\chi_i \phi_i^\Omega(r^\Omega)}{E_i^\Omega - \epsilon} \]
Derivation of the Green’s function

- Introduce Bloch operator

\[(T + V_{eff} + L - \epsilon) \Psi(r) = \chi(r) + L \Psi(r)\]

- Expand solution into the R-matrix basis: \(\Psi(r) = \sum_j c_j \phi_j^\Omega(r)\)

\[c_j = \frac{1}{E_j^\Omega - \epsilon} \left[ \chi_j + \frac{1}{2} \phi_j^\Omega(r_\Omega) \frac{d}{dr} \Psi(r) \bigg|_{r=r_\Omega} \right]\]

\[\chi_j = \int_0^{r_\Omega} \phi_j^\Omega(r) \chi(r) dr\]

- The derivative is determined from the boundary condition at \(r_\Omega\)

\[\frac{d}{dr} \Psi(r) \bigg|_{r=r_\Omega} = \frac{A}{1 - AR_l(\epsilon)} \sum_i \frac{\chi_i \phi_i^\Omega(r_\Omega)}{E_i^\Omega - \epsilon}\]
Final formula for the Green’s function

\[ \Psi(r) = \int_{0}^{r_{\Omega}} G(\epsilon, r, r') \chi(r') dr' \]

\[ G(\epsilon, r, r') = \sum_{i} \frac{\phi_{i}^{\Omega}(r) \phi_{i}^{\Omega}(r')}{E_{i}^{\Omega} - \epsilon} \]

\[ + \frac{A}{2(1 - AR_{l}(\epsilon))} \sum_{i,j} \frac{\phi_{i}^{\Omega}(r) \phi_{i}^{\Omega}(r_{\Omega}) \phi_{j}^{\Omega}(r_{\Omega}) \phi_{j}^{\Omega}(r')}{(E_{i}^{\Omega} - \epsilon)(E_{j}^{\Omega} - \epsilon)} \]

Computational details

- Primary basis – Jacobi polynomials \( P_n^{(0,2)}(z) \)

\[
\int_{-1}^{1} (1 + z)^2 P_n^{(0,2)}(z) P_m^{(0,2)}(z) \, dz \propto \delta_{mn}
\]

\[
\zeta_n(r) = \sqrt{\frac{2n + 3}{r_\Omega^3}} r P_n^{(0,2)} \left( \frac{2r}{r_\Omega} - 1 \right)
\]

\[\zeta_n(0) = 0, \quad \zeta_n(r_\Omega) = \sqrt{\frac{2n + 3}{r_\Omega}}, \quad \frac{d}{dr} \zeta_n(r) \bigg|_{r=r_\Omega} = ?\]

- Provided interaction potential is smooth function of \( r \) the Green's function is smooth and high-order gaussian quadratures can be applied for integration on \((0, r_\Omega)\)
**Convergence properties**

• Constant potential \( V(r) = V_0, \chi(r) = \chi_0 \sin(kr), \epsilon > V_0 \)

\[
\Psi(r) = \sum_j c_j \phi_\Omega^j(r)
\]

![Graph showing precision vs number of basis functions in the expansion of the solution](image)
Convergence properties

- Constant potential $V(r) = V_0$, $\chi(r) = \chi_0 \sin(kr)$, $\epsilon > V_0$

$$\Psi(r) = \sum_j c_j \phi_j^\Omega(r) = \sum_j d_j \zeta_j(r)$$

![Graph showing precision vs. number of basis functions](image)
Application to electron-molecule scattering

\[ |\Psi^{(+)}\rangle = |\Psi_{asym}\rangle + (\epsilon - T_N - V_d(R) + i\epsilon)^{-1} F(\epsilon)|\Psi^{(+)}\rangle \]

- \( F(\epsilon, R, R') \) is a short range energy-dependent non-local complex operator that is difficult to evaluate numerically. It is necessary to reduce number of mesh points as much as possible.

- \( V_d \) is a local long range potential, usually strongly repulsive at short distances.

- In order to determine the vibrational excitation cross section below dissociative attachment threshold Green’s function has to be computed for negative energy.

- Algorithms used for its evaluation has to be stable even in classically forbidden regions, where linearly independent solutions of the homogeneous Schrödinger equation have very different values of magnitude.
Application to electron-molecule scattering

\[ |\Psi^{(+)}\rangle = G_{d}^{(+)}(\epsilon)V_{d}\varepsilon_{i}|\nu_{i}\rangle + G_{d}^{(+)}(\epsilon)F(\epsilon)|\Psi^{(+)}\rangle \]

\[ e^{-} + \text{HBr scattering, VE 0 \rightarrow 1 cross section} \]
Conclusions

- **Diagonalization** of the modified Hamiltonian in the internal region is done only once. The energy dependence of the Green’s function is explicit in the final formula.

- Numerical effort can be further reduced by **dividing the interval** $(0, r_\Omega)$ into several sectors as is usually done in the R-matrix propagation technique.

- Use of **Jacobi polynomials** for the primary basis guarantee **high accuracy** of the numerical solution.

- **R-matrix** representation of the Green’s function is **stable and accurate** even in classically forbidden regions.

- Compared to old approach $(G_d(\epsilon, R, R') = \frac{2}{k} u_l(R_<) v_l(R_>)$, trapezoidal integration rule) the **time demands** for the solution of Lippmann-Schwinger equation describing nuclear dynamics were reduced to approximately 10%. The accuracy was increased to about 7 significant digits.