Calculation of interaction-induced spectra using complex absorbing potentials

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Outline

- What is collision-induced absorption?
- The complication with rotational degrees of freedom
- Possible solution: absorbing potential
- Description of the method
- Test: H–He spectrum
Collision-induced absorption

Example: H–He gas mixture

- $\mu$ is the collision-induced dipole
- like a rotational transition (in the far infrared)
- dumbbell angular momentum selection rule: $\ell_f = \ell_i \pm 1$
- short collision time $\Rightarrow$ quasi-continuous spectra
- source of opacity in atmospheres of planets and cool stars
Why theoretical investigation?

- Need absolute absorption for modelling of stellar and planetary atmospheres
- Measurements:
  - The absorption is weak
  - Sparse temperature grid
- Want to understand the underlying molecular interactions
Collision-induced absorption with molecules

e.g. $\text{H}_2$–$\text{H}_2$:

Account for rotational degrees of freedom

$\text{H}_2$–$\text{H}_2$ at 77 K requires scattering calculations with about 40 coupled channels

More channels for heavier species ($\text{N}_2$, $\text{CH}_4$, etc.)

The coupled scattering equations are integrated towards large separations $R$ (say 200 bohrs)

The physics happens where $R$ is small (say < 10 bohrs)
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Can one make the integration range smaller?
Complex absorbing potentials

- Commonly used in time-dependent quantum calculations
- Here the approach is time-independent

Consequences:
- The Schrödinger equation may be solved in small region of $R$
- Free states become pseudo-bound
- Hamiltonian is non-hermitian $\Rightarrow$ complex eigenvalues

Furthermore:
- Dipole–radiation interaction ($\mu \cdot E$) is included in the Hamiltonian (Mies and Julienne $\sim 1982$)
- Collision-induced absorption cross section is computed from:
  - pseudo-bound wave functions
  - complex eigenenergies
  - spherical bessel functions
Hamiltonian matrix

Two atoms colliding in a photon field with frequency $\omega$:

$$H_{nn'}^{\ell\ell'} = \left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dR^2} + \frac{\hbar^2 \ell(\ell + 1)}{2mR^2} + V(R) - n\hbar\omega \right\} \delta_{nn'} \delta_{\ell\ell'}$$

$$+ \sqrt{\frac{2\pi\hbar\omega\phi}{c}} (-1)^{\ell_{\max}} \sqrt{\frac{\ell_{\max}}{3}} \mu(R) \delta_{nn'\pm1} \delta_{\ell\ell'\pm1}$$

- $n$ is 0 before and 1 after absorption
- $m$ is the reduced mass
- $V(R)$ is the interaction-potential
- $\mu(R)$ is the interaction-induced dipole
- $\ell_{\max} = \max(\ell, \ell')$
- $\phi$ is the photon flux (photon number per area and time)
Complex absorbing potential

Add to the Hamiltonian

\[ -i \delta_{nn'} \delta_{\ell \ell'} W(R) \]

where

\[ W(R) = \begin{cases} 
\frac{4E_{\text{min}}}{c^2} \left( \frac{1}{(1-x)^2} + \frac{1}{(1+x)^2} - 2 \right) & R_a \leq R < R_{\text{max}} \\
0 & R < R_a 
\end{cases} \]

and

\[ x = \frac{R - R_a}{R_{\text{max}} - R_a} \]

This absorber is transmission-free (Manolopoulos, 2002). 

\( R_{\text{max}} \) is set so that

\[ R_{\text{max}} - R_a = \lambda_{\text{deBroglie}}(E_{\text{min}}) \]
How do the wavefunctions look?

H–He: collision at 0.0023 hartree \( \approx 730 \) Kelvins

\[ R_{\text{min}} = 1.2 \ \text{bohrs} \]
How do the wavefunctions look?

H–He: collision at 0.0023 hartree ≈ 730 Kelvins

\[ V \text{ [hartree]} \]
\[ R \text{ [bohr]} \]

\[ \psi_{\text{scatt}} \]
\[ W(R) \]

\[ R_{\text{min}} = 1.2 \text{ bohrs} \]
\[ R_a = 3.2 \text{ bohrs} \]
\[ R_{\text{max}} = 9 \text{ bohrs} \]
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![Graph showing wavefunctions](image)

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Solving the radial Schrödinger equation

Discrete variable representation (Light et al. 1985) with uniform grid

\[ \Delta R = \frac{(R_{\text{max}} - R_{\text{min}})}{N}, \quad R_\alpha = R_{\text{min}} + \alpha \cdot \Delta R, \quad \alpha = 1, 2\ldots(N - 1) \]

and associated Fourier functions gives the Hamiltonian

\[ H_{\ell n \alpha}^{\ell' n' \alpha'} = T_{\alpha \alpha'} \delta_{nn'} \delta_{\ell \ell'} + \left\{ \frac{\hbar^2 \ell (\ell + 1)}{2mR_{\alpha}^2} + V(R_\alpha) - n\hbar \omega - iW(R_\alpha) \right\} \delta_{nn'} \delta_{\ell \ell'} \delta_{\alpha \alpha'} \]

\[ + \sqrt{\frac{2\pi \hbar \omega \phi}{c}} (-1)^{\ell_{\text{max}}} \sqrt{\frac{\ell_{\text{max}}}{3}} \mu(R_\alpha) \delta_{nn'} \pm 1 \delta_{\ell \ell'} \pm 1 \delta_{\alpha \alpha'} \]

with the kinetic energy matrix

\[ T_{\alpha \alpha'} = \frac{\hbar^2}{2m \Delta R^2} (-1)^{\alpha - \alpha'} \left\{ \frac{\pi^2}{3} - \frac{2}{2\alpha^2} \right\} \frac{2}{(\alpha - \alpha')^2 - (\alpha + \alpha')^2} \]

\[ \alpha = \alpha' \]
\[ \alpha \neq \alpha' \]

\[ \Rightarrow 2(N - 1) \text{ eigenvectors } \Psi_k \text{ with complex eigenenergies } E_k - i\Gamma_k/2 \]
Obtaining the $S$-matrix

For dipole transition

$$S_{\ell\ell'}(E) = i\Phi_{\ell 0}^T W G^+ W \Phi_{\ell' 1}$$

$$W = W(R_\alpha) \delta_{\alpha\alpha'}$$

$$\Phi_{\ell n} = \{\Phi_{\ell n\alpha}\} = 2 \sqrt{\frac{\Delta R m}{\hbar^2 k_n}} \cdot k_n R_\alpha \cdot j_\ell(k_n R_\alpha)$$

$j_\ell$ is a spherical bessel function

$$k_n = \sqrt{\frac{2m}{\hbar^2}}(E + n\hbar \omega)$$

$$G^+ = \sum_{k=1}^{2N-2} \frac{\Psi_k \Psi_k^T}{E - E_k + i\Gamma_k/2}$$

is the Green’s function matrix
And finally...

the absorption coeefficient

\[
\alpha(\omega, T) = \rho_1 \rho_2 \lambda_0^3 \frac{1 - e^{-\hbar \omega / k_B T}}{\phi h} \int_0^\infty dE e^{-E/k_B T} \sum_{\ell \ell'} |S_{\ell \ell'}(E)|^2
\]

- \(\rho_1, \rho_2\) = number densities of atoms of type 1 and 2
- \(\lambda_0\) = thermal de Broglie wave length
Test: H–He collision-induced absorption

![Graph showing absorption cross-section as a function of frequency for H–He collisions at 1500 K and 3000 K.](image)

- **Curves:** Calculation with absorbing potential
- **Dots:** Conventional scattering calculation \((R_{\text{max}} > 40 \text{ bohrs})\)

Parameters for absorbing potential calculation:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Grid range (R_{\text{min}}) (bohr)</th>
<th>Grid range (R_{\text{max}}) (bohr)</th>
<th>Absorbing potential (R_a) (bohr)</th>
<th>Absorbing potential (R_{\text{max}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500 K(^a) and 3000 K</td>
<td>1.2</td>
<td>9.0</td>
<td>3.2</td>
<td>9.0</td>
</tr>
<tr>
<td>1500 K(^b)</td>
<td>1.2</td>
<td>12.0</td>
<td>6.2</td>
<td>12.0</td>
</tr>
</tbody>
</table>
Conclusion

- Successfull implementation of the complex absorbing potential method in collision-induced absorption by pairs of atoms
- The spatial range could be limited to 9 and 12 bohrs in the test calculations

Outlook:
- Natural description for both bound and free states – dimer contributions next
- Other scattering problems? collisional broadening?
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