Development of CAP-MCSCF method to study the shape resonances for atoms and molecules

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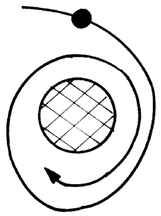
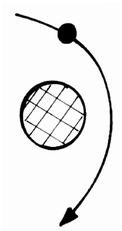
What is scattering resonances?



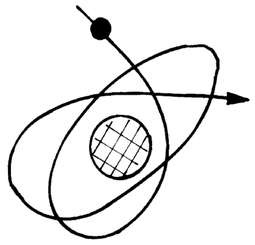
Bound state

Ψ_{bound}
is quadratically-integrable
and vanishes at $x \to \infty$



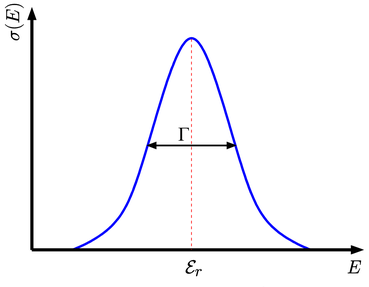
Scattered state

Ψ_{scat}
is not quadratically-integrable and does not vanish at $x \to \infty$



Resonance state

Ψ_{res}
looks like standing wave near the target but behaves like free particle at large distances



Resonance position: $\mathcal{E}_r$
Resonance width: Γ

$$\sigma(E) \propto \rho(E) = \frac{1}{\pi} \frac{\Gamma/2}{(E - \mathcal{E}_r)^2 + (\Gamma/2)^2}$$

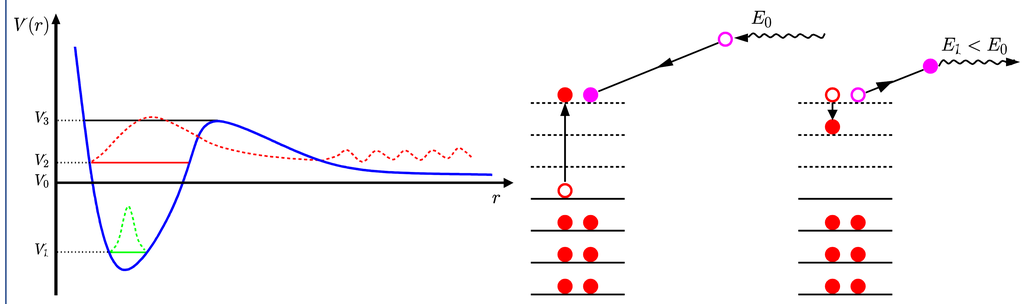
Resonance properties

- Resonance eigenfunction: e^{ikx} (Siegert function)
- For resonances *k* is complex and lies in fourth coordinate of complex *k*-plane
- Time-independent solution diverges as e^{-cx}, where *c=Im k*
- Resonance energy is complex

$$\varepsilon = \mathcal{E}_r - i\,\Gamma/2$$

- Time-dependent solution decays as $e^{-\Gamma t/2\hbar}$

Different kinds of resonances



Shape resonance

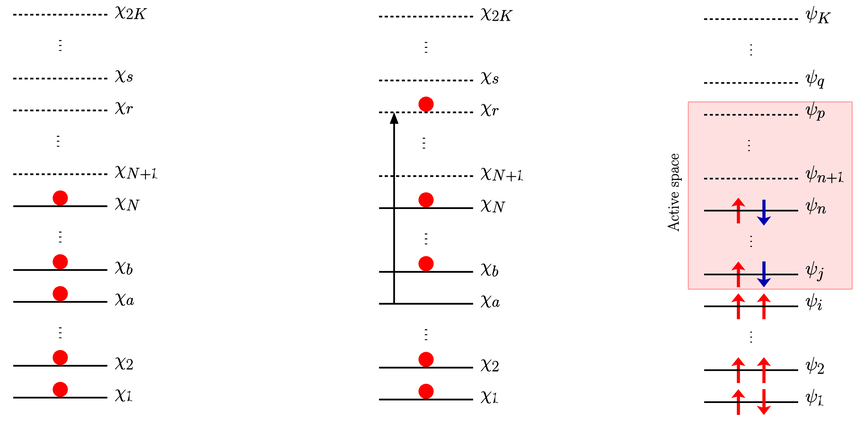
Feshbach resonance

Electronic structure methods

$$\hat{H}_{\text{atom}} = \hat{T}_e + \hat{V}_{en} + \hat{V}_{ee} \qquad \hat{H}_{\text{mol}} = \hat{T}_e + \hat{T}_n + \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn}$$

$$\chi_{2i-1}(x) = \psi_i(r)\alpha(\omega) \qquad \chi_i\text{: spin-orbital}$$

$$\chi_{2i}(x) = \psi_i(r)\beta(\omega) \qquad \psi_i\text{: spatial-orbital}$$



Hartree-Fock method

Full CI method

MCSCF method

- **Hartree-Fock**: Single Slater determinant (SD) based method, ignores large correlation effects
- **Full CI**: Multi SD based method, accounts for all correlation effects
- **MCSCF**: Accounts for static and some dynamic correlations. SDs are generated by distributing electrons among the orbitals in the active space
- Accuracy: Full CI > MCSCF >> Hartree-Fock
- Computational cost: Full CI >> MCSCF > Hartree-Fock

Complex absorbing potential method (CAP)

$$\hat{H}_{\text{CAP}}(\eta) = \hat{H} - i\eta\hat{W}$$

$$W = w_1(x) + w_2(y) + w_3(z)$$

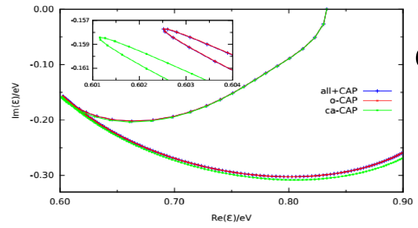
$$w_1(x) = \begin{cases} 0 & \text{if } X_L \le x \le X_R \\ (x - X_L)^2 & \text{if } x < X_L \\ (x - X_R)^2 & \text{if } x > X_R \end{cases}$$

At $\eta = \eta_{opt}$ $\quad \left|\eta \frac{d\varepsilon}{d\eta}\right| = \min$

Appropriate to study molecular resonances under Born-Oppenheimer approximation

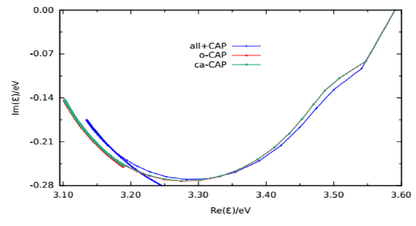
CAP-MCSCF in action

Be^- shape resonance



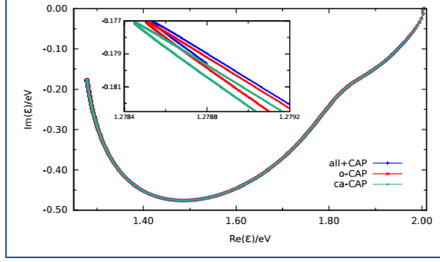
Basis: [14s,11p]
CAS: 2s, 2p,3s
$\mathcal{E}_r$= 0.60 eV
Γ = 0.32 eV

N_2^- shape resonance



$R_{\text{NN}} = 2.074\ au$
Basis: [4s,11p]
CAS: 1π, 3σ, 1π*, 3σ
$\mathcal{E}_r = 0.31$ eV
Γ = 0.29 eV

CO^- shape resonance



$R_{\text{CO}} = 2.132\ au$
Basis: [4s,9p]
CAS: 5σ, 1π, 2π, 6σ
$\mathcal{E}_r = 1.28$ eV
Γ = 0.35 eV

Conclusions

- A new MCSCF method was developed in which the Hamiltonian is perturbed by a CAP
- Thorough investigations on real systems gave very accurate results