Cold Molecules: Theory

Bimalendu Deb

Indian Association for the Cultivation of Science, Kolkata

Email: msbd@iacs.res.in

Contents of the First Lecture:

A. **Introduction to Alkali dimers: Structure and spectroscopy**
B. **Molecular states close to the dissociation limit**
C. **Photoassociation-I (PA)**

Contents of the Second Lecture

A. **Photoassociation-II**
B. **Feshbach resonance (FR)**
C. **Formation of cold molecules by FR and PA**

Cold Molecules: Theory

LECTURE-I

A. Introduction to Alkali dimers: Structure and spectroscopy

A-1. Diatomic molecule: Rigid rotator and symmetric top

A-2. Different coupling schemes: Hund's cases

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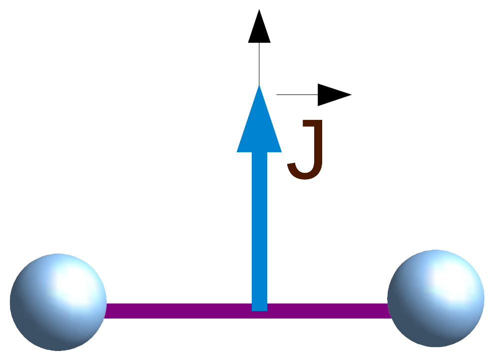
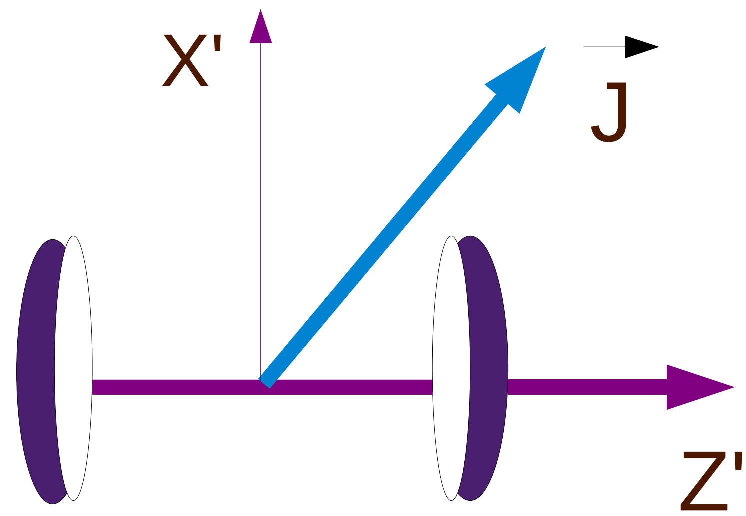
A-1. Diatomic molecule: Rigid rotator and symmetric top

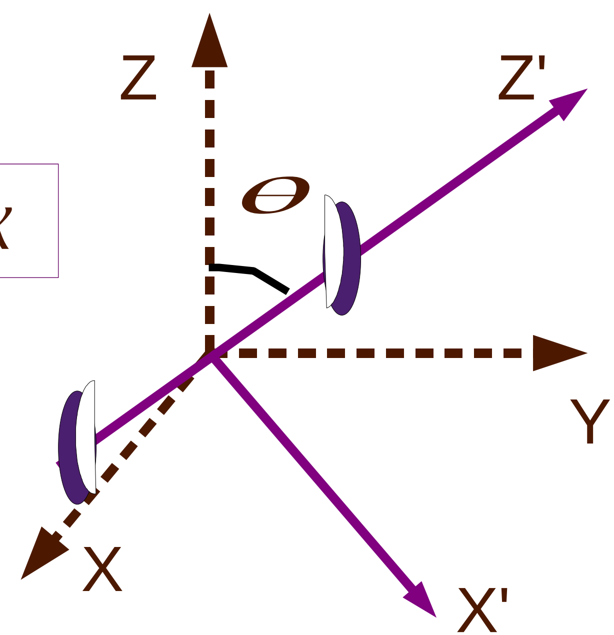




Space-fixed axes: X-Y-Z <-------> Body-fixed axes X'-Y'-Z'

Symmetric Top: Three Euler angles ------------> $\theta,\ \phi,\ \chi$

$$E_{J,K}=\frac{\hbar^2}{2}\left[\frac{J(J+1)}{A}+K^2\left(\frac{1}{C}-\frac{1}{A}\right)\right]$$



Moment of inertia: **C** (internuclear axis) and **A** (perpendicular axis)

Degeneracy:

Angular state →

$$\psi_{JMK}=i^J\sqrt{\frac{2J+1}{8\pi^2}}D_{KM}^{(J)}(\theta,\phi,\chi)$$

$$2M+1 \quad \text{if } K=0$$

$$4M+2 \quad \text{if } K\neq 0$$

$$E_{J,K}=\frac{\hbar^2}{2}\left[\frac{J(J+1)}{A}+K^2\left(\frac{1}{C}-\frac{1}{A}\right)\right]$$

Consider orbital angular motion of electrons

Diatom of two Alkali atoms A and B

Valence electrons 1 and 2

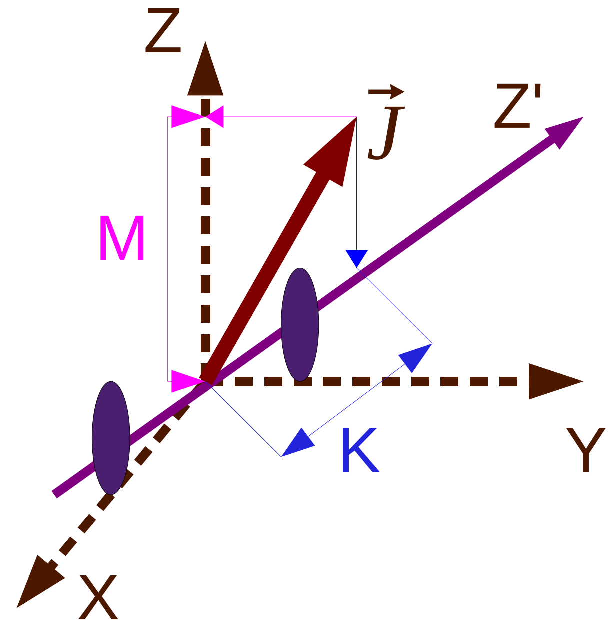
$$J_Z=M \qquad J_{Z'}=K$$

J, M and K : good quantum numbers

$$\vec{L}=\vec{L}_1+\vec{L}_2 \qquad K\equiv L_{Z'}=\Lambda \qquad \vec{J}=\vec{L}+\vec{N}$$

$N \Rightarrow$ rotation of internuclear axis

$$\Lambda=0 \;\Rightarrow\; \Sigma,\quad \Lambda=1 \;\Rightarrow\; \Pi,\quad \Lambda=2 \;\Rightarrow\; \Delta$$



Reflection Symmetry:

Reflection on plane through axis

$$\Rightarrow \quad \Pi,\Delta \qquad\qquad \Sigma^{\pm}$$

Ref: Pauling and Wilson, Quantum Mechanics

Homo-nuclear diatom: Center of symmetry

Invert coordinates x', y', z' of all electrons
-->
Electronic wavefunction is either symmetric (g) or antisymmetric (u)

$$\Rightarrow \ \Sigma_g^{\pm}, \ \Sigma_u^{\pm}, \ \Pi_g, \ \Pi_u, \ \Delta_g, \ \Delta_u$$

Electron spin

$\vec{S}_1 + \vec{S}_2 = \vec{S}$ $\quad S_{Z'}$ known as Σ is a good quantum number if spin-orbit coupling is much weaker than spin-axis coupling

Spin multiplicity: For Alkali dimers, it is either 1 (S=0) or 3 (S=1)
Singlet (S=0) is antisymmetric while triplet is symmetric

$$J_{Z'} = \Omega = \Lambda + \Sigma$$

How are $\vec{L}$ and $\vec{S}$ coupled to molecular axis? $\Rightarrow$ Hund's cases

A-2. Different coupling schemes: Hund's cases

Case (a): Both Λ and Σ are good, $J^2 = \Omega^2 + N^2$

Symbol: ${}^s\Sigma^{\pm.}$, ${}^s\Sigma_c^{\pm.}$, ${}^s\Pi$, ${}^s\Pi_c$, ${}^s\Delta$, ${}^s\Delta_c$ $\quad s \equiv 1,3 \quad c \equiv g,u$

Precision of $\vec{L}$ and $\vec{S}$ about Z'-axis is much faster than nutation

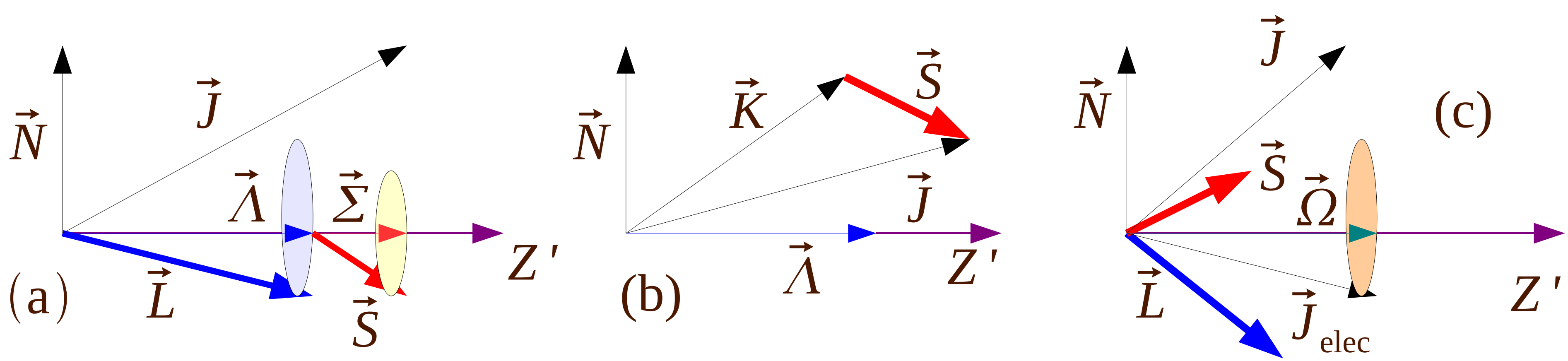
Case (b): Λ is good, $\vec{J} = \vec{K} + \vec{S} = (\vec{\Lambda} + \vec{N}) + \vec{S}$

Precision of $\vec{K}$ and $\vec{S}$ about $\vec{J}$ slower than nutation

Case (c): Neither Λ nor Σ is defined, $\Omega = (\vec{L} + \vec{S})_{Z'}$ is good, Symbol: $|\Omega|_c$

Note: (i) if $\Lambda = 0$ cases (a) and (b) are equivalent

(ii) $J \geq \Omega$, $|\vec{J}| = \sqrt{J(J+1)}$, $|\vec{\Lambda}| = \Lambda$ (iii) $\vec{N}$ is perpendicular to Z'



A-3. Homo- Vs. hetero-nulear molecules

Homo: Nuclei of equal charges --> Non-polar molecule

Hetero: Nuclei of unequal charges --> Polar molecule

Homo: Center of symmetry (g,u); Hetero --> No center of symmetry

A-4. Born-Oppenheimer potentials

Born approximation--> decoupling of electronic and nuclear motion

Reason--> electrons move much faster than nuclei

$$H = H_{\text{elec}} + H_{\text{nuclei}} + H^{\text{Coulomb}}_{\text{elec-nuclei}} + H^{\text{spin-spin}}_{\text{elec-nuclei}}$$

$$H_{\text{elec}} = H^{\text{kinetic}}_{\text{elec}} + H^{\text{spin-orbit}}_{elec} + H^{\text{Coulomb}}_{\text{elec-elec}} \qquad H_{\text{nuclei}} = H^{\text{kinetic}}_{\text{nuclei}} + H^{\text{Coulomb}}_{\text{nuclei-nuclei}}$$

First solve the problem for electrons' motion assuming fixed nuclei with internuclear separation r as a parameter $\Rightarrow$ electronic eigenvalues depend on r $\Rightarrow$ These eigenvalues act as adiabatic B-O potentials for nuclear motion

A-5. Ground and excited molecular states

Ground state is formed from two $S(l=0)$ atoms $\Rightarrow$ belongs to Hund's case (b)

$\Rightarrow$ Singlet $(S=0)$ $^1\Sigma_g$ and triplet $(S=1)$ $^3\Sigma_u$ B-O potentials

Short-range $(r<20\,a_0)$ part depends on overlap and exchange interaction

$\Rightarrow$ Heitler-London theory of binding of neutral atoms

Long-range part depends on multipole Coulomb interaction of two atoms

Long-rane potential of two ground-state (S) atoms

Instantaneous interaction: $\Rightarrow$ $V_{\text{perturb}} = V_{\text{dip-dip}} + V_{\text{dip-quad}} + V_{quad-quad} + V_{\text{dip-oct}} + \cdots$

Second-order perturbation $\Rightarrow$ $V_{\text{long-range}} = -\dfrac{C_6}{r^6} - \dfrac{C_8}{r^8} - \dfrac{C_{10}}{r^{10}}$

Excited state potential:

Excited state is formed from at least one excited atom

Excited molecule composed of $S + P$ atoms is of relevance for PA

Homonuclear excited molecule: $V_{\text{long-range}} \simeq \dfrac{C_3}{r^3}$

Hetero-nuclear (polar) molecule: $V_{\text{long-range}} \simeq \dfrac{\tilde{C}_6}{r^6}$

$$V^{\text{inst}}_{\text{dip-dip}} = \frac{1}{r^3}\left[\vec{d}_1.\vec{d}_2 - 3(\vec{d}_1.\hat{r})(\vec{d}_2.\hat{r})\right] = \frac{A_{\text{dip-dip}}}{r^3} \Rightarrow \text{perturbation}, \quad \vec{d}_i = -\mathrm{e}\sum_i \vec{r}_i$$

$$A_{\text{dip-dip}} = \mathrm{e}^2\left(x_1 x_2 + y_1 y_2 - 2 z_1 z_2\right), \quad A_{\text{dip-dip}} \Rightarrow \text{quadratic in electron coordinates}$$

$$V_{\text{dip-quad}} = \frac{A_{\text{dip-quad}}}{r^4}, \quad A_{\text{dip-quad}} \Rightarrow \text{cubic in electron coordinates}$$

$$V_{\text{dip-quad}} = \frac{A_{\text{quad-quad}}}{r^5}, \quad A_{\text{quad-quad}} \Rightarrow \text{quartic in electron coordinates}$$

van der Waal's potential between two S atoms

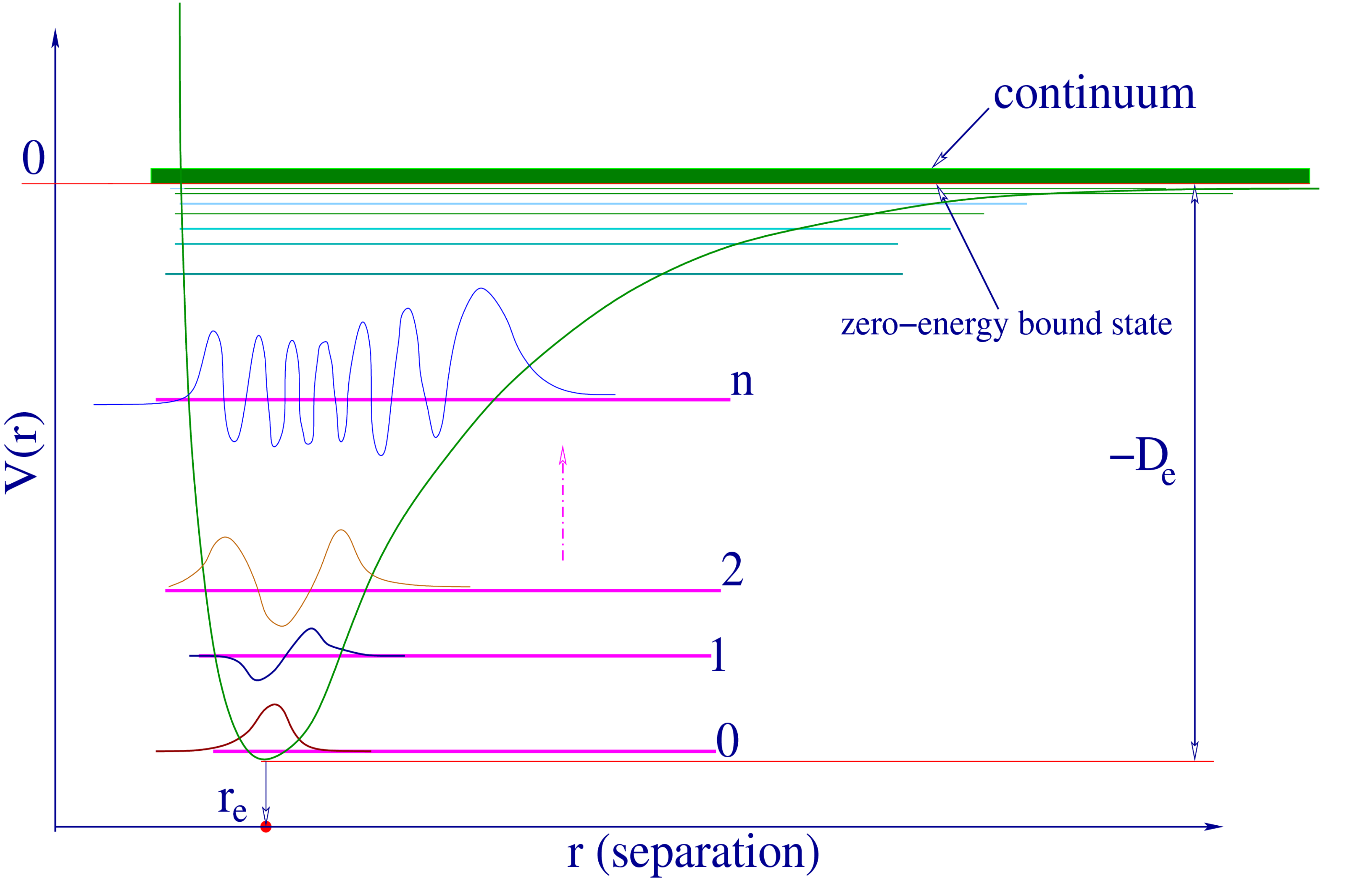
2nd order perturbation $\Rightarrow$ $V_{\text{long-range}} = \frac{1}{r^6}\frac{\left|A^{\text{gr}\to\text{ex}}_{\text{dip-dip}}\right|^2}{E_{\text{gr}} - E_{\text{ex}}}$ $\Rightarrow$ Attractive since $E_{\text{gr}} < E_{\text{ex}}$

Ground state $\Rightarrow$ two S-atoms, excited state $\Rightarrow$ two P-atoms

$\Rightarrow$ separated atom basis

Short-range potential : Both electrons can belong to two atoms

--> Heitler-London theory--> direct and exchange overlap



continuum
0
zero−energy bound state
n
V(r)
−D$_e$
2
1
0
r$_e$
r (separation)

A-6. Electronic, vibrational and rotational spectra

Electronic energy --> equilibrium position of potential

Energy scales: Electronic energy >> Vibrational energy >> rotational energy

Typically, $E_{\mathrm{elec}} \sim 10^3$ to $10^4\,\mathrm{cm}^{-1}$, $E_{\mathrm{vib}} \sim 50$ to $100\,\mathrm{cm}^{-1}$, $1\ \mathrm{cm}^{-1} \simeq 30\ \mathrm{GHz}$

In the first approximation $\psi = \underbrace{\psi_{\mathrm{elec}}^{\mathrm{space}}\ \psi_{\mathrm{elec}}^{\mathrm{spin}}}_{\psi_{\mathrm{elec}}}\ \underbrace{\psi_{\mathrm{vib}}\ \psi_{\mathrm{rot}}\ \psi_{\mathrm{nucl}}^{\mathrm{spin}}}_{\psi_{\mathrm{nucl}}}$

Selection rules:

Transition electric dipole moment matrix element $M_{\psi\psi'} = \int d^3r\, \psi'(-e\vec{r})\psi$

Vibrational selection --> Franck-Condon principle

Electronic and rotational selection --> Symmetry

NOTE: Dipole moment is an odd functions of electron coordinates

Inversion symmetry (parity): $+ \Leftrightarrow -$ $\Rightarrow$ reflection through plane with Z'

Homo-nuclear molecule

Center of symmetry: $g \Leftrightarrow u$ How is related to parity ?

Selection rule for rotational states:

$\Delta J = \pm 1, 0 \quad \Rightarrow$ follows from wavefunctions of symmetric top

$\Delta J = \pm 1 \;\Rightarrow$ holds for rigid rotator

$$\Delta L = \pm 1$$

Electron spin selection rule: $\Delta S = 0$

Nuclear inversion symmetry: $P\left(\psi_{\mathrm{rot}} \psi_{\mathrm{nucl}}^{\mathrm{spin}}\right) \Rightarrow \left(-1\right)^{J} \left(-1\right)^{I+1}$ remains unchanged

$\Rightarrow$ Even and odd J have different intensities due to nuclear spin symmetry

Other selection rules:

$$\Delta M' = \pm 1, 0 \;\Rightarrow \Delta \Lambda = \pm 1, 0 \quad \text{(Hund's cases a and b)}$$

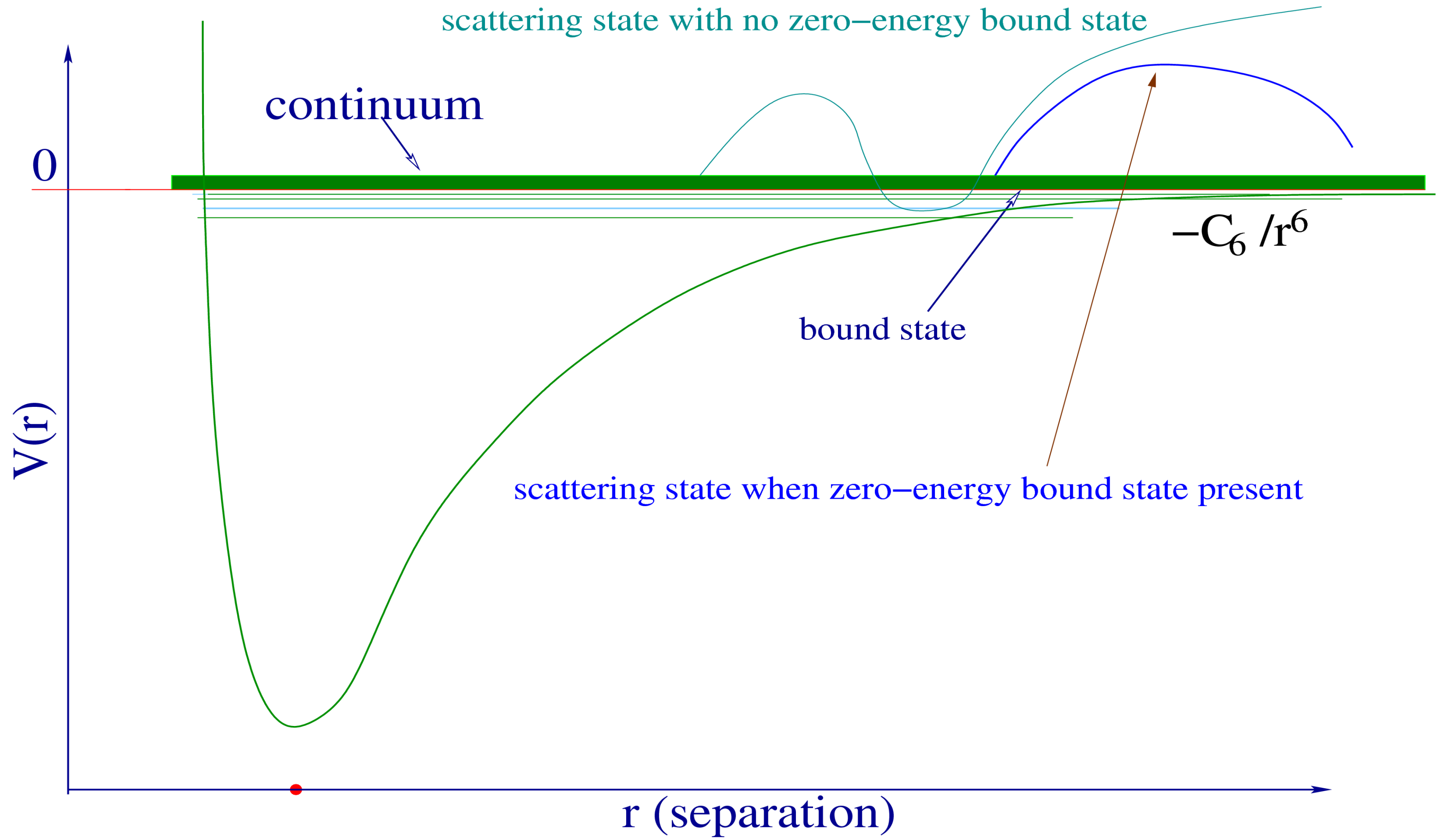
$$\Sigma \rightarrow \Sigma \,\text{Transition}: \quad \Sigma^{+} \rightarrow \Sigma^{+}, \quad \Sigma^{-} \rightarrow \Sigma^{-}$$

Inversion in space-fixed frame $\equiv$ reflection through plane in body-fixed frame

Homo-nuclear molecule: $g \rightarrow u, \quad u \rightarrow g$

Exchange symmetry $\equiv$ Inversion symmetry

- Relationship between low energy scattering states and molecular states close to dissociation limit



B-1: Continuum states at low energy: Wigner threshold laws

B-2: Ground molecular states close to the dissociation limit

The form of boundary cond is true if

$$V(r \to \infty) \to 0 \quad \text{faster than} \quad \pm\frac{1}{r}$$

Differntial scattering cross section $\Rightarrow \dfrac{d\sigma}{d\Omega} = \left|f(\Omega)\right|^2$

Ratio of scattered to incident flux per unit Ω

Flux $\equiv \vec{J}.\hat{r}$, $\vec{J}$ is probability current density

$$\vec{J} = \frac{\hbar}{2\mathrm{m}\,i}\left[\Psi^* \nabla \Psi - \Psi \nabla \Psi^*\right]$$

Elastic scattering $\Rightarrow \left|\vec{k}_i\right| = \left|\vec{k}\right| = k$

Partial wave analysis

Spherically symmetric potential: $V(\vec{r}) \equiv V(|\vec{r}|)$

$$\frac{-\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{L^2}{\hbar^2 r^2}\right]\Psi+V(r)\Psi=E\Psi$$

$$L^2=-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$$[H,L^2]=[H,L_z]=[L^2,L_z]=0$$

$$L^2 Y_{lm}(\theta,\phi)=l(l+1)\hbar^2 Y_{lm}(\theta,\phi)$$

$$L_z Y_{lm}(\theta,\phi)=m\hbar Y_{lm}(\theta,\phi)$$

B-1: Continuum states at low energy: Wigner threshold laws

Two-particle scattering: $\left[\frac{-\hbar^2}{2\mathrm{m}_1}\nabla_1^2 - \frac{\hbar^2}{2\mathrm{m}_2}\nabla_2^2 + V(\vec{r}_1 - \vec{r}_2)\right]\Psi_{12} = E\Psi_{12}$

Relative coordinate: $\vec{r} = \vec{r}_1 - \vec{r}_2,$ reduced particle with mass $m = \frac{m_1 m_2}{m_1 + m_2}$

COM coordinate: $\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}$, COM particle with mass $M = m_1 + m_2$

$$H = H_R + H_r, \quad H_R = \frac{\hbar^2}{2\mathrm{M}}\nabla_R^2, \quad H_r = \frac{-\hbar^2}{2\mathrm{m}}\nabla_r^2 + V(\vec{r}) \;\Rightarrow [H_r, H_R] = 0$$

The equation of relative motion

$$H_r\psi = \frac{-\hbar^2}{2\mathrm{m}}\nabla_r^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r})$$

Scattering $(E \geq 0)$ boundary conditions: $\Psi_{\text{in}}\Psi_{\text{out}} \rightarrow$ free particle states

$$\Psi_{\text{out}}(r \rightarrow \infty) = A\left[\exp(i\vec{k}_i.\vec{r}) + f(\theta, \phi)\frac{\exp(ikr)}{r}\right]$$

$$\exp[i\vec{k}.\vec{r}] = \sum_{l=0}^{\infty} i^l (2l+1) j_l(kr) P_l(\cos\theta)$$

Let $\Psi = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} C_{lm}(k) \Psi_{lm}(k,r) Y_{l,m}$

For convenience define $\phi_{lm}(k,r) = r\,\Psi_{lm}(k,r)$

Then we have

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - U(r) + k^2\right]\phi_l = 0$$

$$U(r) = \frac{2\mathrm{m}\,V(r)}{\hbar^2}, \qquad k^2 = \frac{2\mathrm{mE}}{\hbar^2}$$

When $U(r) = 0$, $\qquad \phi_l \equiv kr\, j_l(kr), \quad kr\, n_l(kr)$

OR,

$$\phi_l \equiv h^{(1)} = j_l + i\,n_l, \qquad h^{(2)} = j_l - i\,n_l$$

$$\lim_{\to 0}(r\,j_l) \sim r^{l+1}, \qquad \lim_{\to 0}(r n_l) \sim r^{-l}$$

Boundary conditions for partial waves

$$\phi_l(r) = r\,A_l(k)\left[j_l - \tan\delta_l(k)\,n_l\right] \sim A_l(k)\sin\left[kr - l\pi/2 + \delta_l(k)\right]$$

$$\phi_l(r) = k\,r\left[D_l(k)\,h^{(1)} + F_l(k)\,h^{(2)}\right]$$

$$\sim \tilde{A}_l(k)\left[-(-1)^l \exp(-i\,kr) + S_l(k)\exp(i\,kr)\right]$$

$$\sim \bar{A}_l(k)\left[\sin(kr - l\pi/2) + T_l(k)\exp(kr - l\pi/2)\right]$$

S-, T- and K-matrices:

$$\Psi_l \sim \frac{\sin(kr - l\pi/2)}{kr} + f_l(k)\frac{\exp(kr - l\pi/2)}{r}$$

$$f_l(k) = \frac{-T_l(k)}{k} = \frac{1}{k}\frac{S_l(k)-1}{2\mathrm{i}} \quad \Rightarrow \quad T_l(k) = \frac{1}{2i}[1 - S_l(k)]$$

$$S_l(k) = \exp[2i\delta_l(k)] \Rightarrow \text{ S-matrix element, } \quad K_l(k) = \frac{1}{2i}\frac{S_l - 1}{S_l + 1} = \tan\delta_l$$

Formally, S = 1 + R, only "R" includes the effect of V(r)

$$\langle \vec{p}\,'|R|\vec{p}\rangle = -2\pi i\,\delta(E_p - E_{p'})\langle \vec{p}\,'|T|\vec{p}\rangle \;\Rightarrow \text{ On-shell T-matrix}$$

Relation between T and G:

$$T = V + VGV, \quad G(z) = (z - H)^{-1} = G^{(0)} + G^{(0)} V G = G^{(0)} + G V G^{(0)}$$

$$\Rightarrow \; T = V + V G^{(0)} T$$

Cold collision

A paradigm model is rectangular well or barrier potential

$$V(r) = \pm V_{0,} \;\; \text{for} \;\; r \le r_0, \quad V(r) = 0, \;\; \text{for} \;\; r > r_0$$

$$k_0 = \frac{\sqrt{2\mathrm{m}(E \mp V_0)}}{\hbar}, \quad k = \frac{\sqrt{2mE}}{\hbar}$$

$$\phi_{\text{out}}(r) = A[\sin(kr) + \tan\delta_0 \cos(kr)], \quad \text{for} \;\; r > r_0$$

$$\phi_{\text{in}}(r) = B \sin(k_0 r), \quad \text{for} \;\; r \le r_0$$

Continuity of in and out states at the boundary

$$\text{At } r = r_0, \quad \text{we have} \quad \left[\frac{1}{\phi_{\text{in}}} \frac{d\phi_{\text{in}}}{dr} \right]_{r=r_0} = \left[\frac{1}{\phi_{\text{out}}} \frac{d\phi_{\text{out}}}{dr} \right]_{r=r_0}$$

$$\Rightarrow \quad k_0 \cot(k_0 r_0) = \frac{k[\cot(k r_0) - \tan\delta_0]}{1 + \tan\delta_0 \cot(k r_0)}$$

$$\Rightarrow \quad \tan\delta_0 = \frac{k\cot(kr_0) - k_0\cot(k_0 r_0)}{k + k_0 \cot(kr_0)\cot(k_0 r_0)}$$

Logarithmic derivative for any parttial wave

$$\frac{d}{dr} \ln[r j_l(k_0 r)]_{r=r_0} = \frac{d}{dr} \ln[r j_l - r n_l \tan\delta_l]_{r=r_0}$$

S-wave phase shift at low energy

$$\tan\delta_0 = \frac{k\cot(kr_0) - k_0\cot(k_0 r_0)}{k + k_0\cot(kr_0)\cot(k_0 r_0)}$$

Low energy limit $\Rightarrow \; k r_0 \ll 1, \quad E \ll V_0$

(a) For $V(r) < 0$ (potential well), $k_0 > k \;\Rightarrow\; \delta_0 > 0$

(b) For $V(r) > 0$, (potential barrier), $k_0 < k \;\Rightarrow\; \delta_0 < 0$

$$\lim_{k\to 0} k\cot\delta_0(k) = \lim_{k\to 0}\left[\frac{[k\cot(k r_0)][k_0\cot(k_0 r_0)]}{k\cot(k r_0) - k_0\cot(k_0 r_0)}\right]$$

$$\lim_{k\to 0} k\cot\delta_0(k) = -\left(\frac{1}{a_s}\right), \quad a_s \text{ is called scattering length}$$

$$\Rightarrow \quad -a_s = \frac{\tan(k_0 r_0)}{k_0} - r_0,$$

$$\lim_{k\to 0} k_0 \simeq \frac{\sqrt{2mV_0}}{\hbar}, \quad k_0 r_0 \ll 1 \;\Rightarrow\; \text{potential is weak}$$

Weakly interacting systems: Effective potential is weak
Potential can be expressed in terms of scattering length

Effective range expansion: H. Bethe

$$\lim_{k\to 0} k \cot\delta(k) \simeq -\frac{1}{a_s} + \frac{1}{2} r_0 k^2$$

$$\text{Unitarity:} \quad f = \frac{1}{k\cot\delta - ik} \;\Rightarrow\; f(k\to 0) = -\frac{a_s}{1 + ika_s}$$

$$k a_s \ll 1 \;\Rightarrow\; \text{low energy}$$

Dilute gas:

$$\Rightarrow\; n a_s^3 \ll 1$$

Wigner Threshold Laws:

$$\lim_{k\to 0}\delta_l(k)\sim k^{2l+1}, \text{ OR } f_l(k)\sim k^{2l} \quad \text{if } V(r)=0, \text{ for } r>r_0$$

For long-range potential of the form $\pm\dfrac{1}{r^n}$

$$\delta_l(k)\sim k^{2l+1}, \text{ if } l<(n-3)/2, \quad \delta_l(k)\sim k^{n-2}, \quad \text{otherwise}$$

$$f_l(k)=-\frac{1}{k}t_l(k)=-\frac{1}{k}\left[\frac{1}{k}\int_0^\infty kr\,j_l(kr)V(r)\phi_l(kr)\,dr\right]$$

$$\phi_l(kr)=kr\,j_l(kr)+\int_0^\infty G_l(rr')V(r')\phi_l(r')\,dr'$$

Prove:

$$G_l(r,r')=-\frac{2\pi}{k}\hat{j}_l(kr_<)\hat{h}_l^+(kr_>)$$

Pseudo-potential: Contact potential

$$V(\vec{r}-\vec{r}\,')=\frac{4\pi\hbar^2 a_s}{m}\delta^3(\vec{r}-\vec{r}\,')$$

$$f_{\vec{k}',\vec{k}}=-\frac{m}{4\pi\hbar^2}\int d^3r'\exp(-i\vec{k}'.\vec{r}\,')V(\vec{r}\,')\psi_{\vec{k}}(\vec{r}\,')$$

$$\psi_{\vec{k}}(\vec{r})=\exp(i\vec{k}.\vec{r})-\frac{m}{4\pi\hbar^2}\int d^3r'\frac{\exp(ik|\vec{r}-\vec{r}\,'|)}{|\vec{r}-\vec{r}\,'|}\psi_{\vec{k}}(\vec{r}\,')$$

$$\psi_{\vec{k}}(\vec{r})\sim\exp(i\vec{k}.\vec{r})+f_{\vec{k}',\vec{k}}\frac{\exp(ikr)}{r}$$

$$f_{\vec{k}',\vec{k}}=-\frac{m}{4\pi\hbar^2}\int d^3r'\exp(-i\vec{k}'.\vec{r}\,')V(\vec{r}\,')\psi_{\vec{k}}(\vec{r}\,')$$

Born approximation

$$f_B(\vec{k}',\vec{k}) = -\frac{m}{4\pi\hbar^2} V_{\vec{k}'-\vec{k}}$$

$$f(k,\theta) = \sum_{l=0}^{\infty} \frac{2l+1}{k} \exp(i\delta_l)\sin\delta_l P_l(\cos\theta)$$

According to Wigner threshold laws, we have

$$\lim_{|\vec{k}|=|\vec{k}'|\to 0} f(\vec{k}',\vec{k}) \simeq -a_s$$

$$\Rightarrow V_{\text{pseudo}}(\vec{r}) = \frac{4\pi\hbar^2 a_s}{m} \int \exp(\vec{k}.\vec{r})\, d^3\vec{k} = \frac{4\pi\hbar^2 a_s}{m} \delta^3(\vec{r})$$

B-2: Molecular states near threshold

Basic theory of bound state formation by cold collision
Near-zero energy bound state

-ve $a_s \Rightarrow$ attractive potential

Large attractive potential $\Rightarrow$ +ve $a_s \Rightarrow$ near-zero energy bound state

$$k_0 r_0 \to \pi/2, \quad \delta_0 \to \pi/2 \Rightarrow \quad a_s \to \infty$$

$$\psi_{\text{bind}} \sim \exp(-\kappa r) \simeq 1 - \kappa r = -\kappa(r - 1/\kappa)$$

$\psi_0^{\text{scat}} \sim r - a_s \Rightarrow \kappa \simeq 1/a_s \Rightarrow$ geometric interpretation of a_s

$\lim_{k\to 0} \delta_0(k) = (n + \frac{1}{2})\pi \Rightarrow$ Levinson's theorem

Cold Molecules

Formation of molecules by cold collision

Two methods: Feshbach resonance and Photoassociation

Resonances --> Quasi-bound states

Two kinds of resonances: Shape & Feshbach

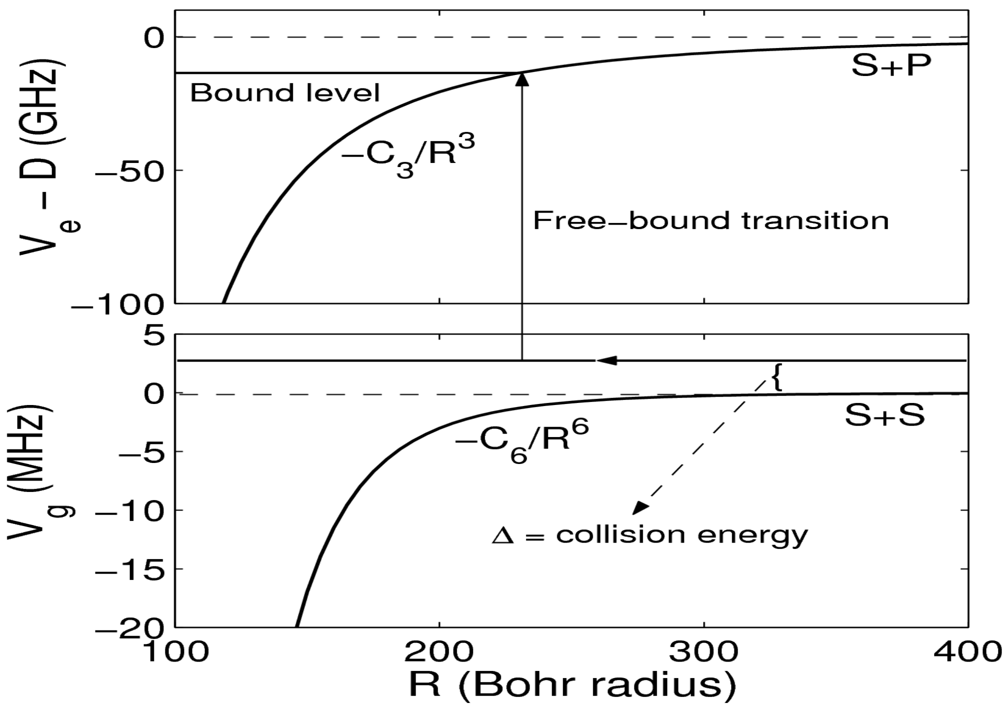
Feshbach resonance (FR) in Nuclear Physics

FR in ultracold atoms: To tune interaction

FR is used to form MBEC, BCS state in Fermi atoms, to explore BEC-BCS crossover, to form Effimov states etc.

C. Photoassociation-I

Importance of PA



Resonant d-d interaction

Precision measurement of interatomic forces

Raman PA spectroscopy: Creation of cold molecule

Photoassociation of BEC: Cold chemistry

Threshold law and selection rule
--> Molecule formed by PA should be rotationally cold

Since atoms need to be cold,
--->molecule formed is also translationally cold

Molecular states formed by PA: Homo- Vs. Hetero-nuclear molecule

Long-range potential due to resonant d-d interaction:
In the separated atom limit --> S+P

Homo-nuclear molecule : 1st order perturbation in d-d interaction is finite
Hetero-nuclear molecule : 1st order perturbation in d-d interaction is zero

Homo-nuclear: $\psi_{\pm}=\frac{1}{\sqrt{2}}\left(\psi_A^S\psi_B^P\pm\psi_A^P\psi_B^S\right) \Rightarrow \langle\psi_{\pm}|\vec{d}_1.\vec{d}_2|\psi_{\pm}\rangle=\langle\vec{d}_1\rangle.\langle\vec{d}_2\rangle$

Hetero-nuclear: $\psi_1=\psi_A^S\psi_B^P$ OR $\psi_2=\psi_A^P\psi_B^S \Rightarrow \langle\psi_i|\vec{d}_1.\vec{d}_2|\psi_i\rangle=0$

$V(r)\sim C_3/r^3$ for an excited molecule composed of two homo-nuclear atoms

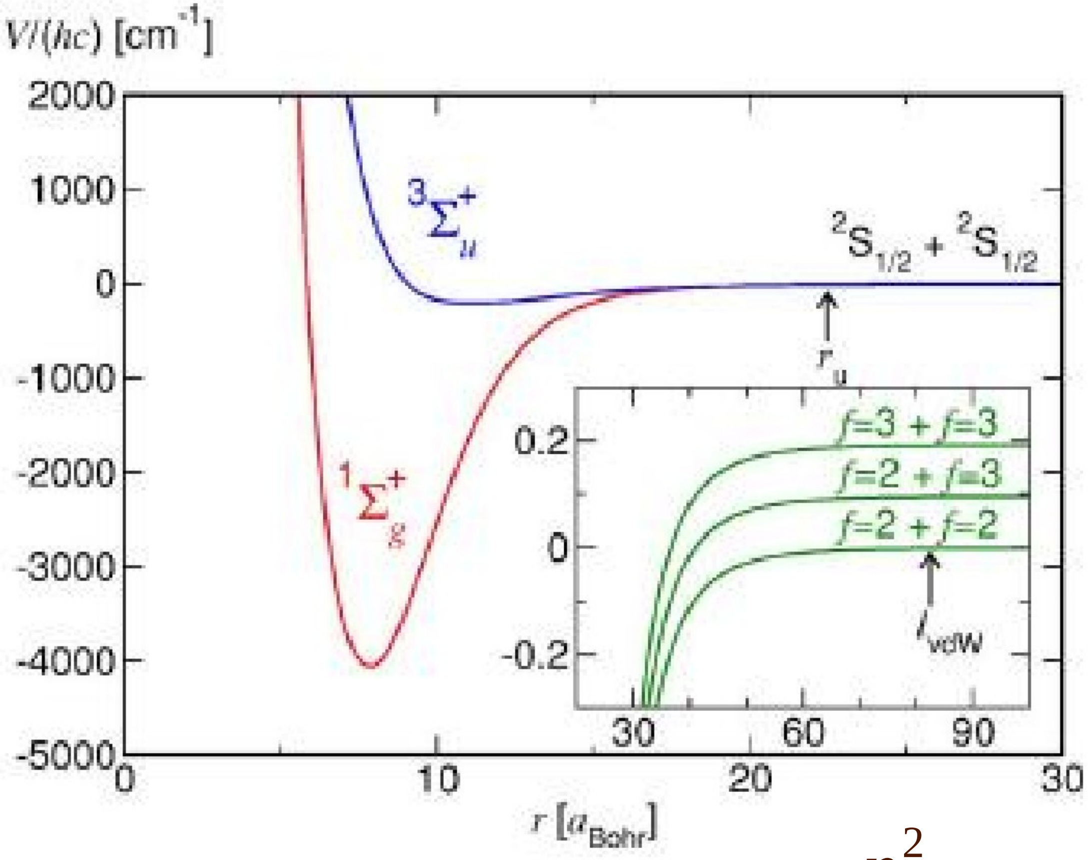
$V(r)\sim C_6/r^6$ for a molecule composed of two hetero-nuclear atoms

Summary and References

A. **Introduction to Alkali dimers: Structure and spectroscopy**

B. **Molecular states close to the dissociation limit**

Magnetic Feshbach resonance



$$H=\frac{p^2}{2m}+\sum_{i=1,2} H_i^{\mathrm{int}}+V^c(r)+V^d(r)$$

$$H_i^{\mathrm{int}}=V_i^{hf}+V_i^z=\frac{a_{\mathrm{hf}}}{\hbar^2}\vec{S}.\vec{I}+\left(\gamma_e S_z-\gamma_n I_z\right)B_z$$

Resonances and bound states

Resonance $\Rightarrow$ A peak in σ Vs E curve

$\Rightarrow \delta(E)$ changes rapidly throught $\pi/2$

Quasi-bound or zero-energy bound state

Shape resonance: nonzero partial wave

Feshbach resonance: Multichannel case

Analyrtic properties of S matrix: Poles of S at comples E or k

$$\Re[k] \to + \text{ ve}, \quad \Im[k] \to 0^- \Rightarrow \text{ Resonance}$$

$$\Re[k] = 0, \quad \Im[k] \to + \text{ ve} \Rightarrow \text{ Bound state}$$

Bound states: Potential well

A pole at $k = k' - i\kappa \Rightarrow E = \dfrac{\hbar^2 k^2}{2\mathrm{m}} = E_r - \dfrac{1}{2} i\Gamma$

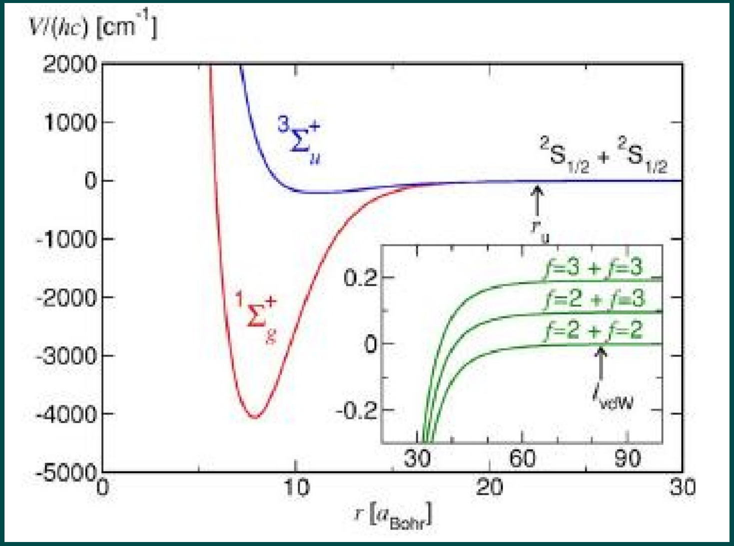
$$\alpha = k_0 r_0, \qquad \beta = k r_0, \qquad A^2 = \frac{V_0}{E_0}, \qquad E_0 = \frac{\hbar^2}{2 m r_0^2}$$

$$S = \exp[2i\delta] = \exp(-2i\beta)\frac{\alpha\cot\alpha + i\beta}{\alpha\cot\alpha - i\beta} = \exp[2i\eta^{\mathrm{out}}]\exp[2i\eta^{\mathrm{in}}]$$

Pole of $S \Rightarrow \alpha\cot\alpha = i\beta$

$$\lim_{A\to 0}\beta_n = n\pi - i\infty$$

Magnetic Feshbach resonance in cold atoms



Tunability of atom-atom interaction

Strongly interacting atomic gases

Formation of metastable cold molecules

Molecular BEC and BEC-BCS crossover

Unitarity limit in scattering: $S_l = 1 + 2ikf_l$

Unitarity $\Rightarrow$ $|1+2ikf_l|^2 = 1$ $\Rightarrow$ $\Im[f_l] = k|f_l|^2 \Rightarrow \Im[1/f_l] = -k$

$f_l = 1/(g_l - ik)$, $\quad g_l = k\cot\delta_l(k)$, At low energy, $f_0 = -\dfrac{a_s}{1+ika_s}$

At resonance, $f_0 \sim \dfrac{i}{k}$, since $ka_s \gg 1$

Combination of hyperfine and Zeeman interaction

$$H = \frac{p^2}{2m} + \sum_{i=1,2} H_i^{\mathrm{int}} + V^c(r) + V^d(r)$$

$$H_i^{\mathrm{int}} = V_i^{hf} + V_i^z = \frac{a_{\mathrm{hf}}}{\hbar^2} \vec{S}.\vec{I} + \left(\gamma_e S_z - \gamma_n I_z\right) B_z$$

$$V^c = V_0(r) P_0 + V_1(r) P_1$$

PA Rate

Rate of loss of atoms: $K_p = \langle v_{\text{rel}} \sigma_p \rangle, \qquad \sigma_p \propto |T_p|^2$

T_p is the scattering T-matrix in the presence of PA laser

Optical Feshbach resonance: Another method of tuning scattering length

Fano interference: PA in the vicinity of magnetic FR

A new tool to study quantum interference in atom-molecule conversion

Coherent atom-molecule dynamics

Lecture-II Cold Molecules: Theory

Contents:

A. PA-II

Continuum-bound dipole transitions
Hyperfine interaction in ground continuum
Transformation from atomic to molecular basis
Multichannel scattering

Continuum-bound dipole interaction

$$H_{\text{atom-field}} = \langle \psi_{\text{continuum}} | (\vec{d}_1 . \vec{E} + \vec{d}_2 . \vec{E}) | \psi_{\text{bound}} \rangle \qquad \vec{d}_i = -\mathrm{e}\,\vec{r}_i$$

Hyperfine interaction important

Hyperfine interaction in ground-state

$$H = T(r) + \sum_{i=\mathrm{A,B}} H^{i}_{\mathrm{hf}} + V^{c} + V^{d}$$

$$T(r) = -\frac{1}{2m}\nabla_r, \qquad V^{d} \Rightarrow \text{magnetic dipole-dipole interaction}$$

$$V^{c} = V_0(r) P_0 + V_1(r) P_1 = \frac{V_0(r) + 3V_1(r)}{4} + (V_1 - V_0)\vec{S}_1 . \vec{S}_2$$

Molecular angular momentum basis: $\vec{S}=\vec{s}_1+\vec{s}_{2,} \quad \vec{I}=\vec{i}_1+\vec{i}_2$

$$\langle S' M'_S; I' M'_I | V^c | S M_S; I M_I \rangle = \delta_{I,I'} \delta_{M_I M'_I} \delta_{S,S'} \delta_{M_S M'_S} V_S$$

$\Rightarrow$ diagonal in molecular basis

$$H_{hf} = \frac{a_{\text{hf}}}{\hbar^2} \vec{s}_j . \vec{i}_j = \frac{a_{\text{hf}}}{2\hbar^2} \left(\vec{f}_j^2 - \vec{s}_j^2 - \vec{i}_j^2 \right) \Rightarrow \text{ diagonal in atomic basis,} \quad \vec{f}_j = \vec{s}_j + \vec{i}_j$$

Molecular hyperfine spin $\vec{f}=\vec{f}_1+\vec{f}_2$

Transformation from atomic to molecular basis $\Rightarrow$

$$\langle f_1 m_1; f_2 m_2 | V^c | f'_1 m'_1; f'_2 m'_2 \rangle = \sum_{S,I,M_S,M_I} V_S \langle (f_1 f_2) f m_f; l m_l | S M_S; I M_I; l' m'_l \rangle$$
$$\times \langle S M_S; I M_I; l' m'_l | (f_1 f_2) f m_f; l m_l \rangle$$

$m_f = m_1 + m_{2,} \ \ \vec{F} = \vec{f} + \vec{l}, \quad M = M_F + m_l; \quad F$ and M_F are good quantum numbers

$$\langle S\,M_S; I\,M_I; l'\,m'_l|(f_1 f_2) f\,m_f; l\,m_l\rangle = \delta_{ll'}\,\delta_{m_l m'_l}\langle S\,M_S; I\,M_I|f\,m_f\rangle$$

$$\times\sqrt{(2f_1+1)(2f_2+1)(2S+1)(2I+1)}\begin{Bmatrix} s_1 & i_1 & f_1 \\ s_2 & i_2 & f_2 \\ S & I & f \end{Bmatrix}\left(\frac{1+(1-\delta_{f_1 f_2})(-1)^{(S+I+l)}}{\sqrt{2-\delta_{f_1 f_2}}}\right)$$

PA spectroscopy: Free-bound or continuum-bound transition

$$H_{\text{atom-field}} = \langle \psi_{\text{continuum}}|(\vec{d}_1.\vec{E}+\vec{d}_2.\vec{E})|\psi_{\text{bound}}\rangle$$

$$\vec{d} \;\Rightarrow\; \text{tensor of rank one, } \vec{d}_{\text{atomic}} \;\rightarrow\; \vec{D}_{\text{molecular}}$$

$$\psi_{\text{continuum}} = \psi_{\text{elec}}^{\text{free}}\,\psi_{\text{angular}}^{\text{free}}\,\psi_{\text{scattering}}, \quad \psi_{\text{bound}} = \psi_{\text{elec}}^{\text{molecular}}\,\psi_{\text{angular}}^{\text{moleculoar}}\,\psi_{\text{vibrational}}$$

Selection rules in continuum-bound transitions

Multichannel scattering: Hyperfine channel

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B. Feshbach resonance

Scattering resonances: Shape vs. multichannel resonances
Multichannel scattering in the presence of a magnetic field
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Resonance phase shift, linewidth, scattering length

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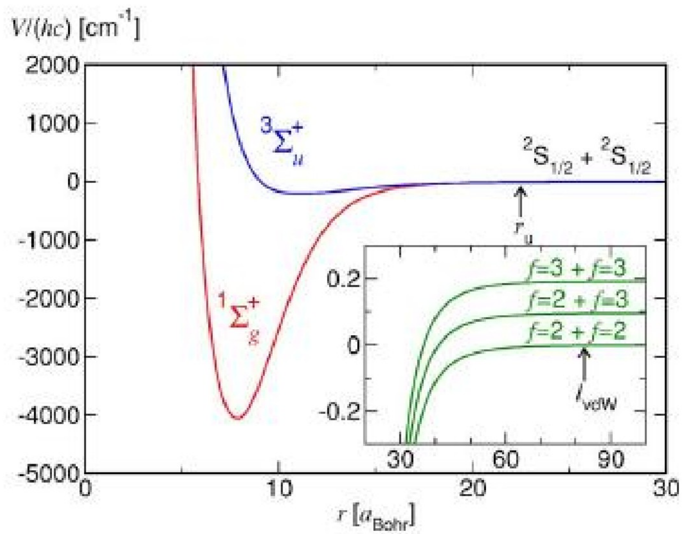

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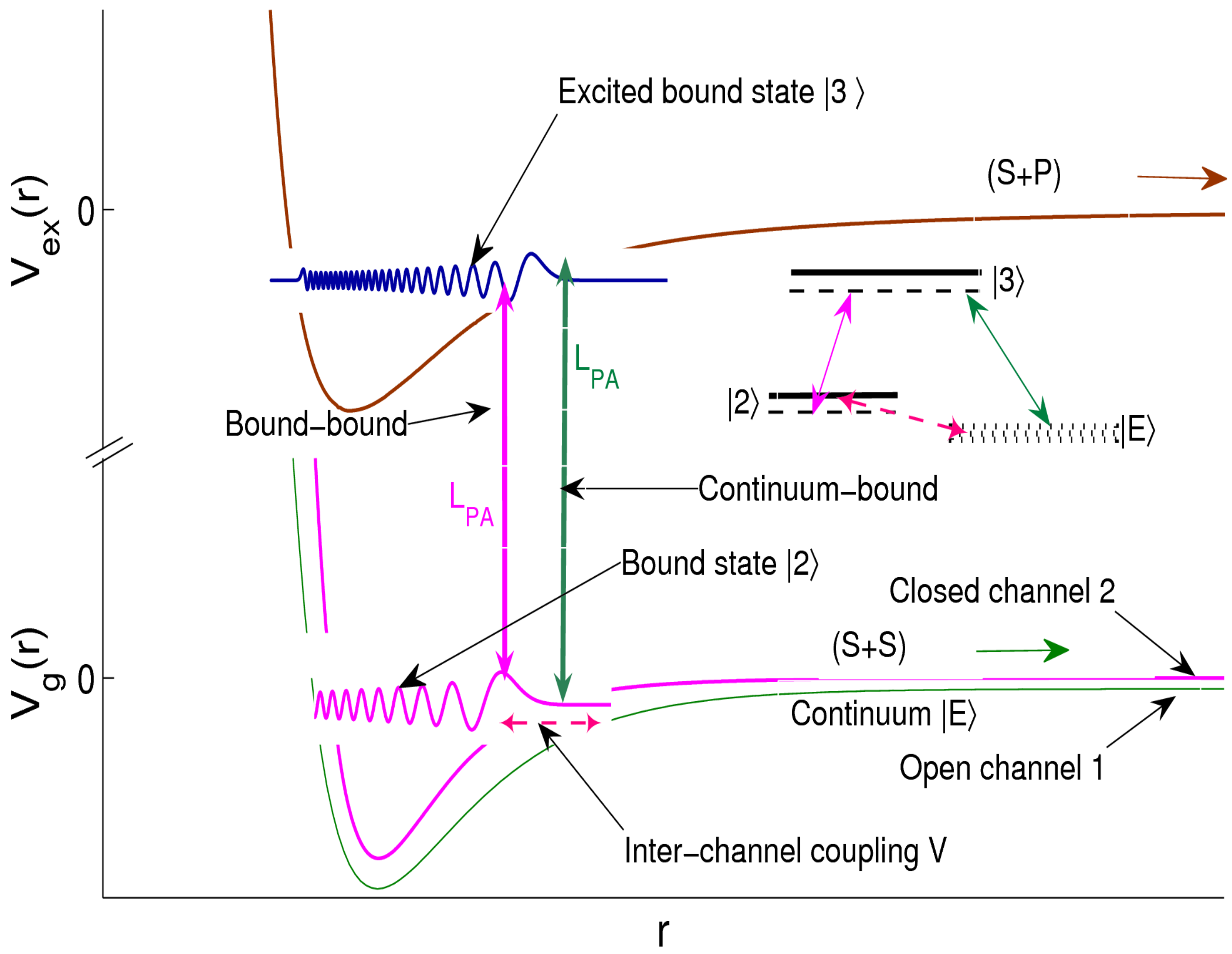
Model of two-channel magnetic Feshbach resonance (MFR)



Two-channel model

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}+V_2(r)-E\right]\phi=-V(r)\chi,$$

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}+V_1(r)-E\right]\chi=-V(r)\phi$$

Introduce Green's functions $G_E(r,r')=-\pi\,\psi_E^{\mathrm{reg}}(r_<)\,\psi_E^{+}(r_>)$

$$G_2(r,r')=-\frac{1}{E-E_0}\phi_0(r)\phi_0(r')$$

$$\phi=\int_0^\infty dr'\frac{\chi(r')V(r')\phi_0(r')}{E-E_0}\ \phi_0(r)=\frac{\tilde{V}_E}{E-E_2}\phi_0(r)$$

$$\chi=\exp(i\eta_0)\psi_E^{\mathrm{reg}}+\frac{\tilde{V}_E}{(E-E_2)}\int dr'G_E(r,r')V(r')\phi_0(r')$$

The solution is

$$\chi(r) = \exp(i\eta_0)\psi_E^{\text{reg}}(r) + \frac{\exp(i\eta_0)V_E}{E - (E_0 + E_{\text{shift}}) + i\Gamma/2}\int dr' G_E(r,r')V(r')\phi_0(r')$$

Asymptotic form $\Rightarrow$ $\chi(r\to\infty) \sim \sin(kr) - T_0 \exp(ikr)$

$$\Rightarrow T_0 = T_0^0 + \exp(2i\eta_0)T_{\text{res}}$$

$$T_{\text{res}} = \frac{\Gamma/2}{E - (E_0 + E_{\text{shift}}) + i\Gamma/2}$$

$$T_0^0 = -e^{i\eta_0}\sin\eta_0$$

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