Reactive collisions of molecules in external fields

Roman Krems
University of British Columbia

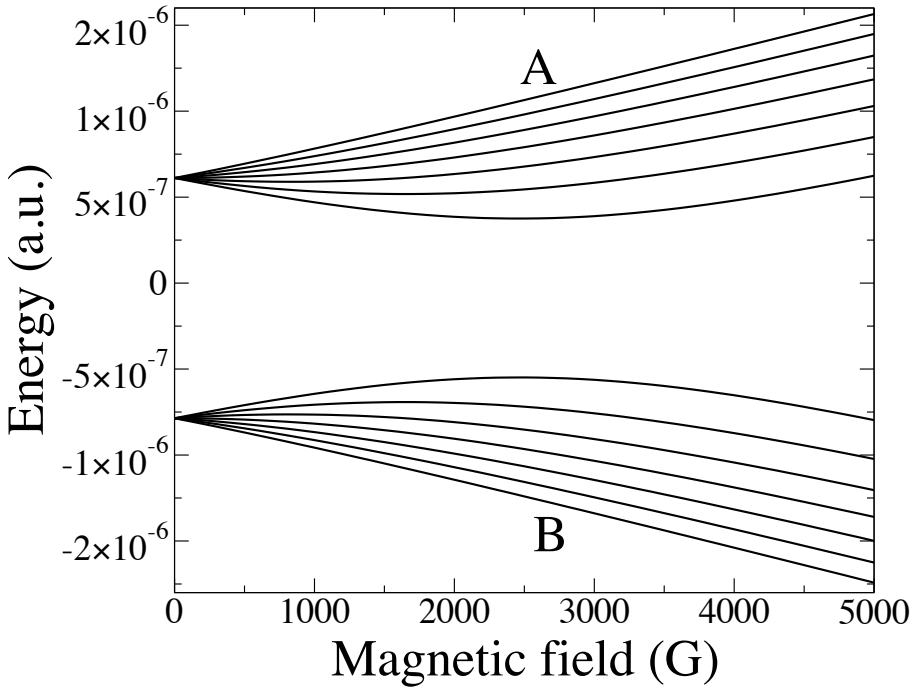
Sergey Alyabyshev
Chris Hemming
Felipe Herrera
Zhiying Li → UBC Physics
Marina Litinskaya
Timur Tscherbul → Harvard University
Erik Abrahamsson → UBC Physics

Funding:

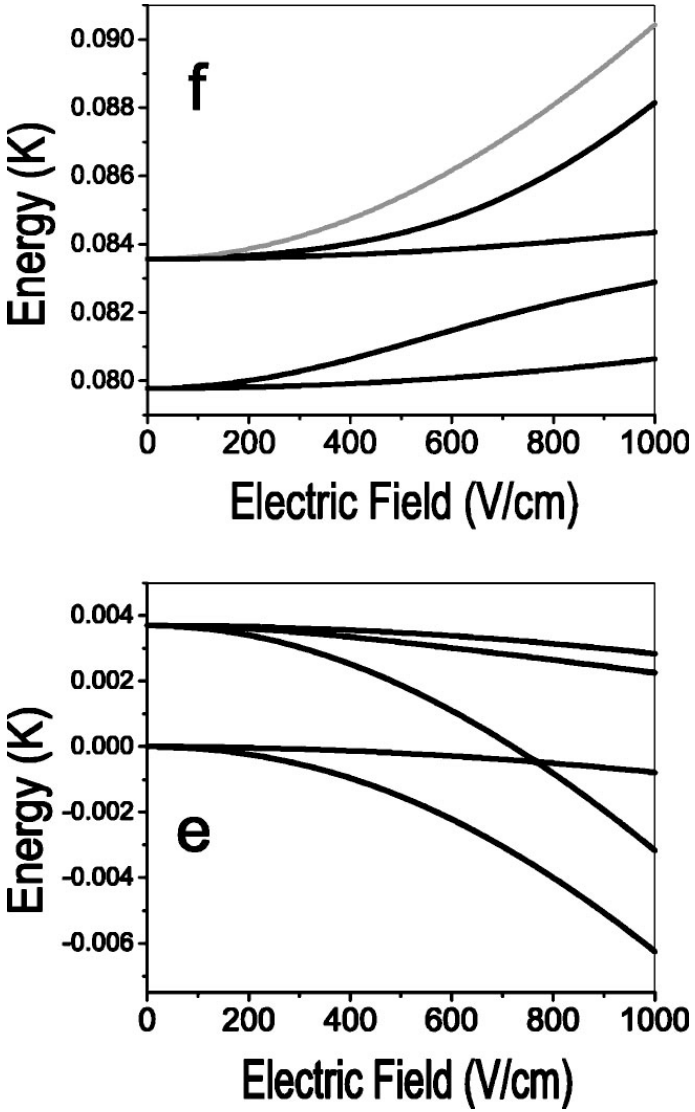
NSERC CRSNG
Canada Foundation for Innovation
Fondation canadienne pour l'innovation
British Columbia
The Best Place on Earth
Les Fiducies Killam Trusts
Peter Wall Institute for Advanced Studies
CRUCS
Canadian Centre for Research on Ultra-Cold Systems

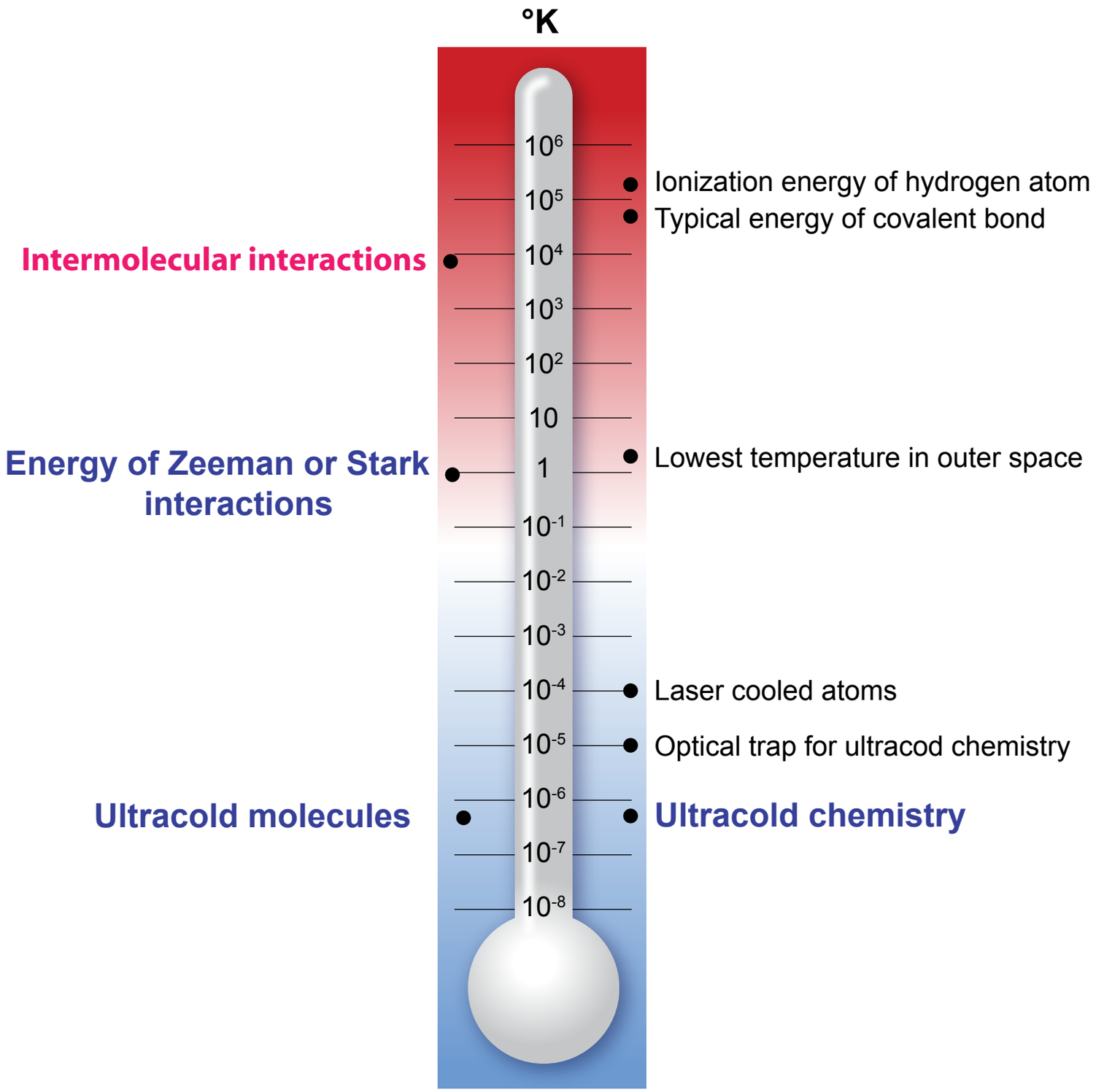
Is there universality in molecular collisions at finite temperature?

Cs atom in magnetic field:



OH molecule in electric field:



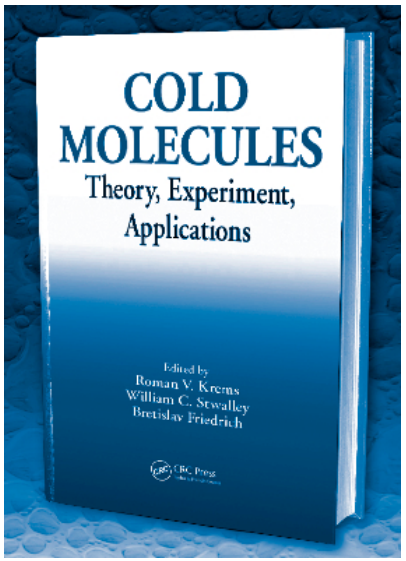

°K
10^{6}
10^{5}
10^{4}
10^{3}
10^{2}
10
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
Intermolecular interactions
Energy of Zeeman or Stark interactions
Ultracold molecules
Ionization energy of hydrogen atom
Typical energy of covalent bond
Lowest temperature in outer space
Laser cooled atoms
Optical trap for ultracod chemistry
Ultracold chemistry

Applications of ultracold molecules:

Cold and Ultracold Molecules: Science, Technology, and Applications,
L. Carr, D. DeMille, R. V. Krems, and J. Ye,
New Journal of Physics 11, 055049 (2009).

Cold Controlled Chemistry,
R. V. Krems,
Physical Chemistry Chemical Physics 10, 4079 (2008).

Quo vadis, cold molecules?
J. Doyle, B. Friedrich, R. V. Krems, and F. Masnou-Seeuws,
European Physical Journal D 31, 149 (2004).



Thermal isolation = confinement of molecules
by dc electric, magnetic or laser fields

Thermal isolation = confinement of molecules
by dc electric, magnetic or laser fields

Cooling experiments = molecular collisions
in external field traps

Thermal isolation = confinement of molecules
by dc electric, magnetic or laser fields

Cooling experiments = molecular collisions
in external field traps

Elastic collisions lead to cooling
Reactive collisions lead to trap loss

Thermal isolation = confinement of molecules
by dc electric, magnetic or laser fields

Cooling experiments = molecular collisions
in external field traps

Elastic collisions lead to cooling
Reactive collisions lead to trap loss

It is critical to understand the effects of
external fields on elastic, inelastic and
chemically reactive collisions of molecules
at cold (~1 K) and ultracold (< 0.001 K) temperatures

Collision theory – basic approach:

Collision theory – basic approach:

$$H = H_{\mathrm{A}} + H_{\mathrm{B}} + V$$

$$H\Psi = E\Psi$$

Collision theory – basic approach:

$$H = H_{\mathrm{A}} + H_{\mathrm{B}} + V$$

$$H\Psi = E\Psi$$

$$\Psi = \sum_i \sum_j F_{ij} \phi_i^{\mathrm{A}} \phi_j^{\mathrm{B}}$$

Collision theory – basic approach:

$$H = H_{\mathrm{A}} + H_{\mathrm{B}} + V$$

$$H\Psi = E\Psi$$

$$\Psi = \sum_i \sum_j F_{ij} \phi_i^{\mathrm{A}} \phi_j^{\mathrm{B}}$$

Compute ϕ^{A} and ϕ^{B} in the *molecule-fixed coordinate frame*

Collision theory – basic approach:

$$H = H_{\mathrm{A}} + H_{\mathrm{B}} + V$$

$$H\Psi = E\Psi$$

$$\Psi = \sum_i \sum_j F_{ij} \phi_i^{\mathrm{A}} \phi_j^{\mathrm{B}}$$

Compute ϕ^{A} and ϕ^{B} in the *molecule-fixed coordinate frame*

Couple **all** angular momenta to re-write

Collision theory – basic approach:

$$H = H_{\mathrm{A}} + H_{\mathrm{B}} + V$$

$$H\Psi = E\Psi$$

$$\Psi = \sum_i \sum_j F_{ij} \phi_i^{\mathrm{A}} \phi_j^{\mathrm{B}}$$

Compute ϕ^{A} and ϕ^{B} in the *molecule-fixed coordinate frame*

Couple **all** angular momenta to re-write

$$\Psi = \sum_J \sum_i \sum_j C_{Jij} \psi_{ij}^J (\phi^{\mathrm{A}} \phi^{\mathrm{B}})$$

Collision theory – basic approach:

$$H = H_{\mathrm{A}} + H_{\mathrm{B}} + V$$

$$H\Psi = E\Psi$$

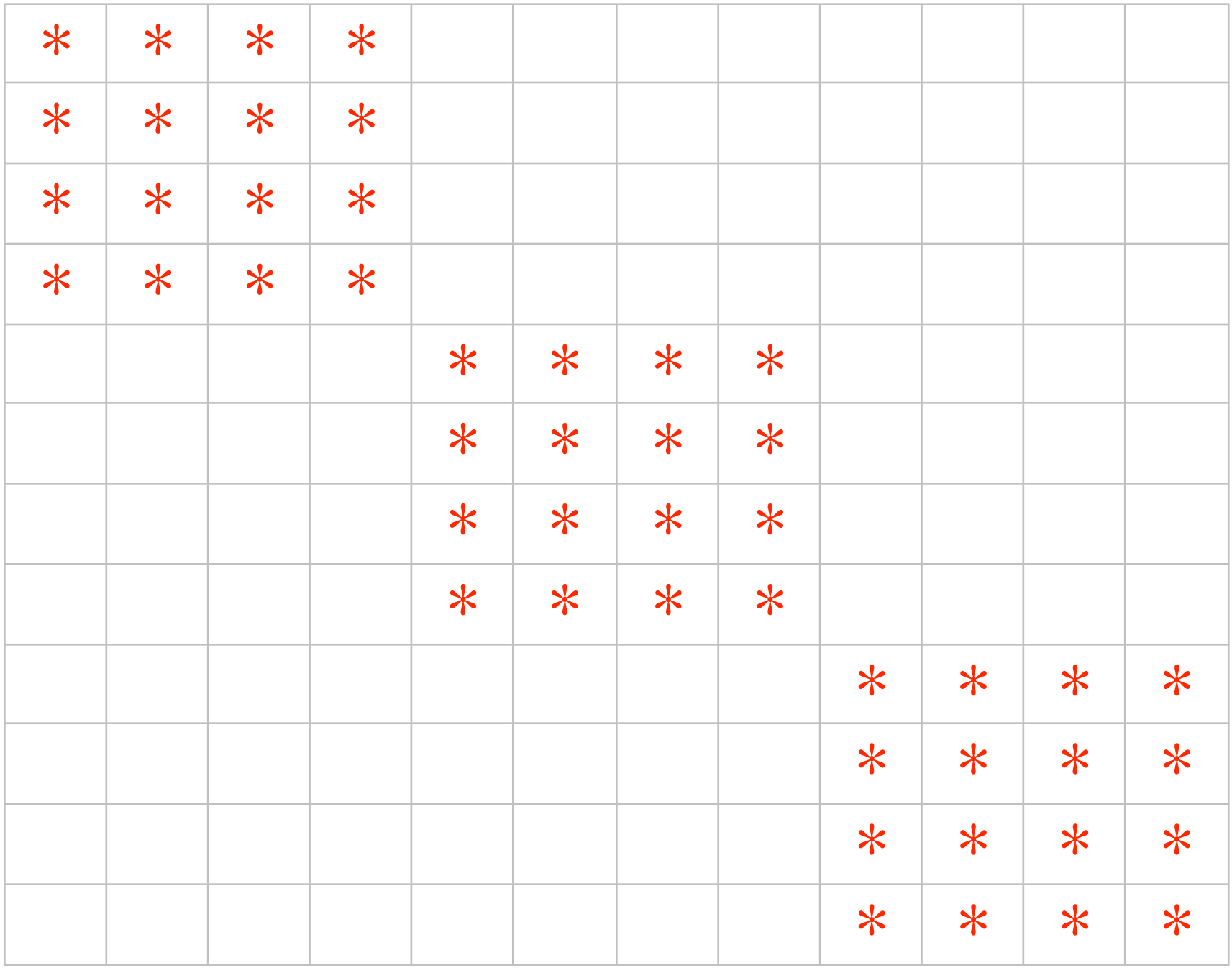
$$\Psi = \sum_i \sum_j F_{ij} \phi_i^{\mathrm{A}} \phi_j^{\mathrm{B}}$$

Compute ϕ^{A} and ϕ^{B} in the *molecule-fixed coordinate frame*
Couple **all** angular momenta to re-write

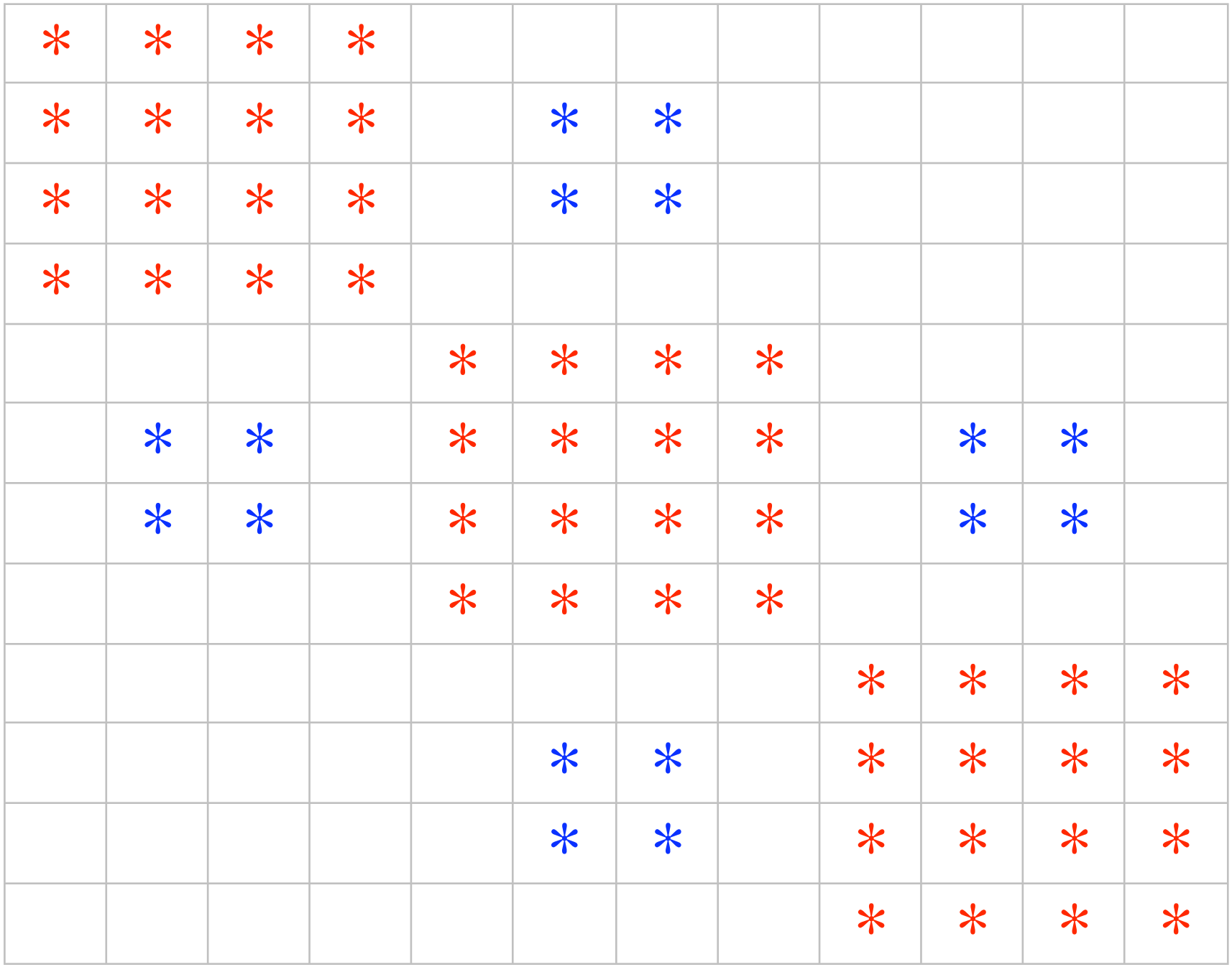
$$\Psi = \sum_J \sum_i \sum_j C_{Jij} \psi_{ij}^J (\phi^{\mathrm{A}} \phi^{\mathrm{B}})$$

Since 1960, this is called Arthurs-Dalgarno representation

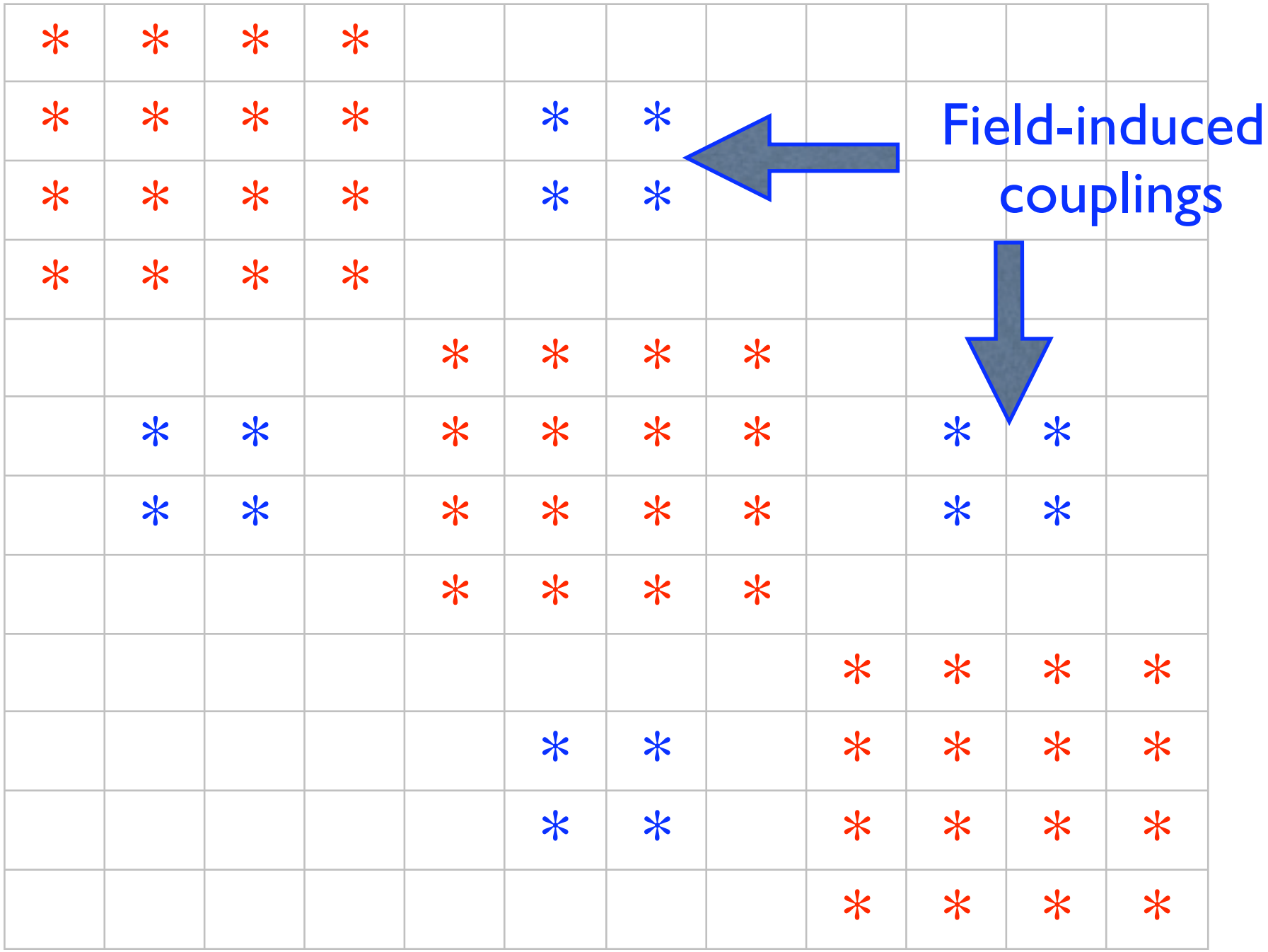
H-matrix in the Arthurs-Dalgarno representation



Hamiltonian in the presence of an external field



Hamiltonian in the presence of an external field



$$H = H_{\mathrm{A}} + H_{\mathrm{B}} + V$$

$$H\Psi = E\Psi$$

$$\Psi = \sum_i \sum_j F_{ij} \phi_i^{\mathrm{A}} \phi_j^{\mathrm{B}}$$

Compute ϕ^{A} and ϕ^{B} in the *molecule-fixed coordinate frame*

Couple **all** angular momenta to re-write

$$\Psi = \sum_J \sum_i \sum_j C_{Jij} \psi_{ij}^J (\phi^{\mathrm{A}} \phi^{\mathrm{B}})$$

Since 1960, this is called Arthurs-Dalgarno representation

$$H = H_{\mathrm{A}} + H_{\mathrm{B}} + V$$

$$H\Psi = E\Psi$$

$$\Psi = \sum_i \sum_j F_{ij} \phi_i^{\mathrm{A}} \phi_j^{\mathrm{B}}$$

Compute ϕ^{A} and ϕ^{B} in the *molecule-fixed coordinate frame*

Couple **all** angular momenta to re-write

$$\Psi = \sum_J \sum_i \sum_j C_{Jij} \psi_{ij}^J (\phi^{\mathrm{A}} \phi^{\mathrm{B}})$$

Since 1960, this is called Arthurs-Dalgarno representation

$$H = H_{\mathrm{A}} + H_{\mathrm{B}} + V$$

$$H\Psi = E\Psi$$

$$\Psi = \sum_i \sum_j F_{ij} \phi_i^{\mathrm{A}} \phi_j^{\mathrm{B}}$$

space-fixed coordinate frame

Compute ϕ^{A} and ϕ^{B} in the ~~*molecule fixed coordinate frame*~~

Couple **all** angular momenta to re-write

$$\Psi = \sum_J \sum_i \sum_j C_{Jij} \psi_{ij}^J (\phi^{\mathrm{A}} \phi^{\mathrm{B}})$$

Since 1960, this is called Arthurs-Dalgarno representation

Fully uncoupled space-fixed representation - example:

Collision of two molecules in the $^2\Sigma$ state

$$\Psi = \sum_i F_i \phi_i$$

$$\phi_i = |N_\mathrm{A} M_{N_\mathrm{A}}\rangle |S_\mathrm{A} M_{S_\mathrm{A}}\rangle |N_\mathrm{B} M_{N_\mathrm{B}}\rangle |S_\mathrm{B} M_{S_\mathrm{B}}\rangle |l m_l\rangle$$

where all the momenta are projected onto the field axis.

R. V. Krems and A. Dalgarno, JCP 120, 2296 (2004).

Fully uncoupled space-fixed representation - example:

Collision of two molecules in the $^2\Sigma$ state

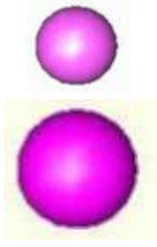
$$\Psi = \sum_i F_i \phi_i$$

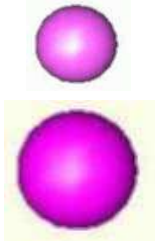
$$\phi_i = |N_\mathrm{A} M_{N_\mathrm{A}}\rangle |S_\mathrm{A} M_{S_\mathrm{A}}\rangle |N_\mathrm{B} M_{N_\mathrm{B}}\rangle |S_\mathrm{B} M_{S_\mathrm{B}}\rangle |l m_l\rangle$$

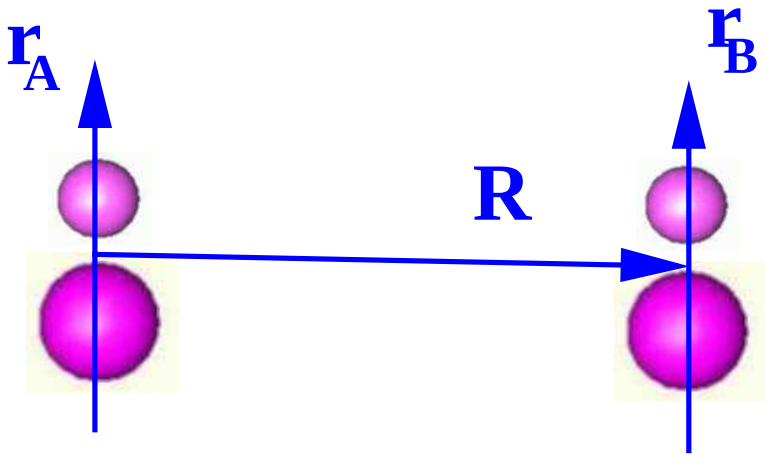
where all the momenta are projected onto the field axis.

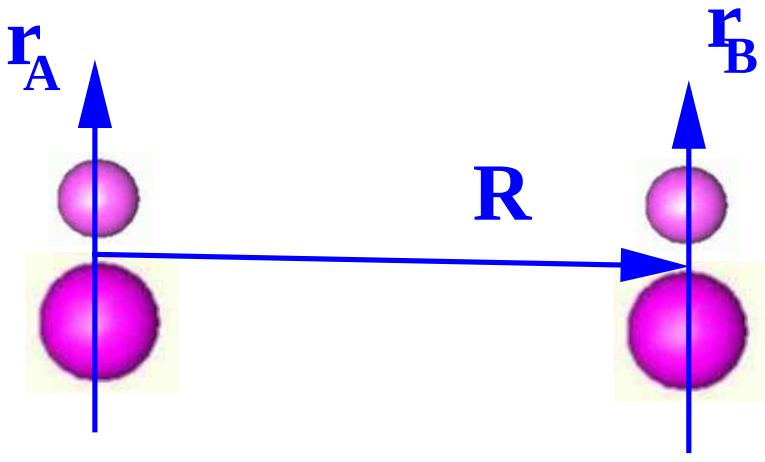
In order to evaluate the matrix of H, all terms in the Hamiltonian must be written in the *space-fixed coordinate frame*.

R. V. Krems and A. Dalgarno, JCP 120, 2296 (2004).






r_A
r_B
R



$$V_{\mathrm{AB}}(\mathbf{R},\mathbf{r}_{\mathrm{A}},\mathbf{r}_{\mathrm{B}}) = (4\pi)^{3/2} \sum_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda} V_{\lambda_{\mathrm{A}}\lambda_{\mathrm{B}}\lambda}(R, r_{\mathrm{A}}, r_{\mathrm{B}})$$

$$\times \sum_{m_{\lambda_{\mathrm{A}}} m_{\lambda_{\mathrm{B}}} m_{\lambda}} \begin{pmatrix} \lambda_{\mathrm{A}} & \lambda_{\mathrm{B}} & \lambda \\ m_{\lambda_{\mathrm{A}}} & m_{\lambda_{\mathrm{B}}} & m_{\lambda} \end{pmatrix} Y_{\lambda_{\mathrm{A}} m_{\lambda_{\mathrm{A}}}}(\hat{r}_{\mathrm{A}}) Y_{\lambda_{\mathrm{B}} m_{\lambda_{\mathrm{B}}}}(\hat{r}_{\mathrm{B}}) Y_{\lambda m_{\lambda}}(\hat{R})$$

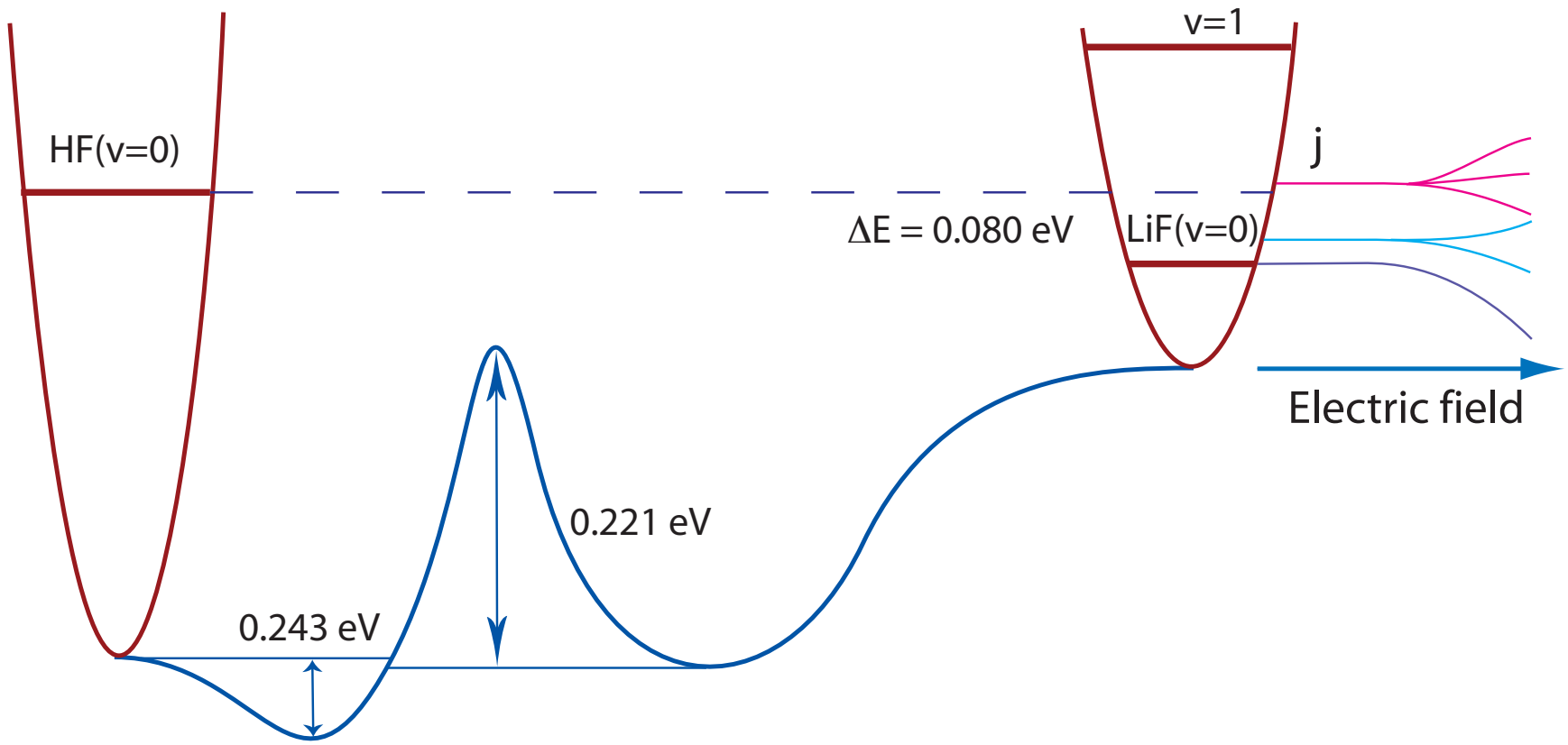
Any interaction in the Hamiltonian can be represented as a direct product of spherical tensors defined in the space-fixed coordinate frame

Any interaction in the Hamiltonian can be represented as a direct product of spherical tensors defined in the space-fixed coordinate frame

The collision problem of molecules in external fields is most conveniently formulated in the fully uncoupled space-fixed representation

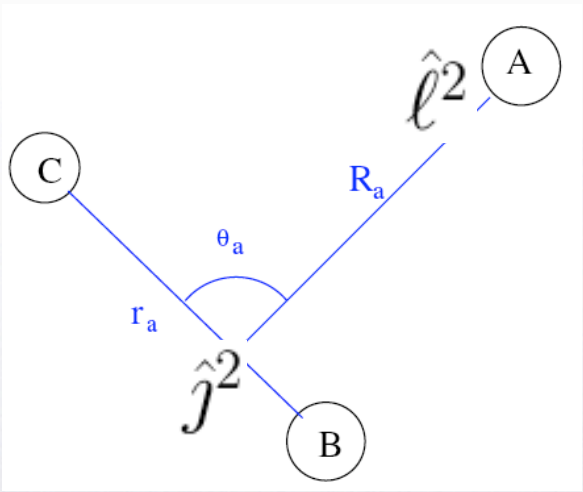
$$\mathrm{Li} + \mathrm{HF} \rightarrow \mathrm{LiF} + \mathrm{H}$$

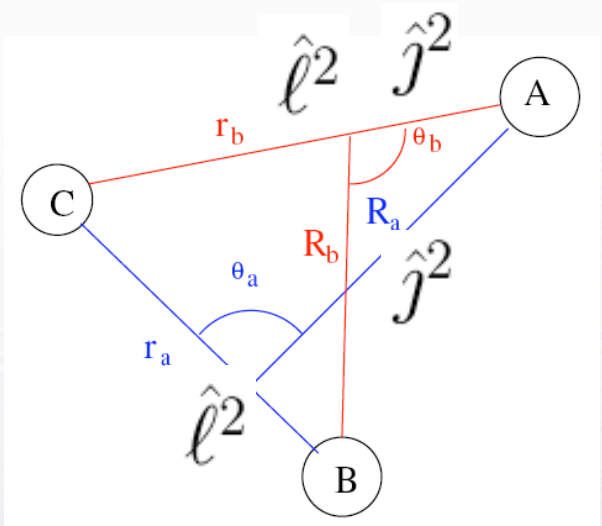
Energy diagram of the reaction Li + HF(v=0, j=0)

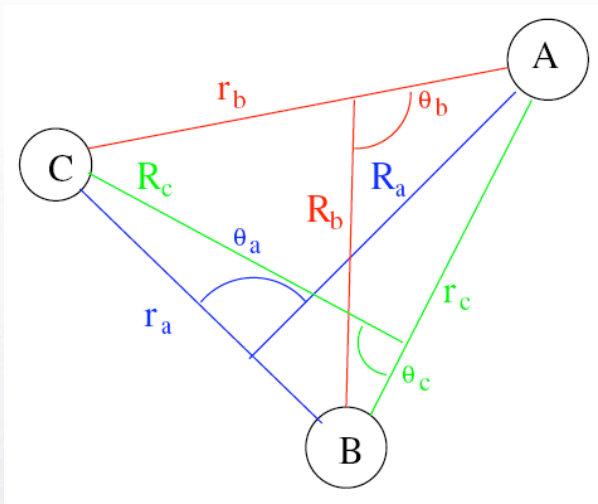


The problem with Jacobi coordinates

$$\hat{H} = -\frac{1}{2\mu}\frac{d^2}{dR^2} - \frac{1}{2m}\frac{d^2}{dr^2} + \frac{\hat{\ell}^2}{2\mu R^2} + \frac{\hat{j}^2}{2mr^2} + V(r, R, \theta)$$







Solution: the *hyperspherical* coordinates

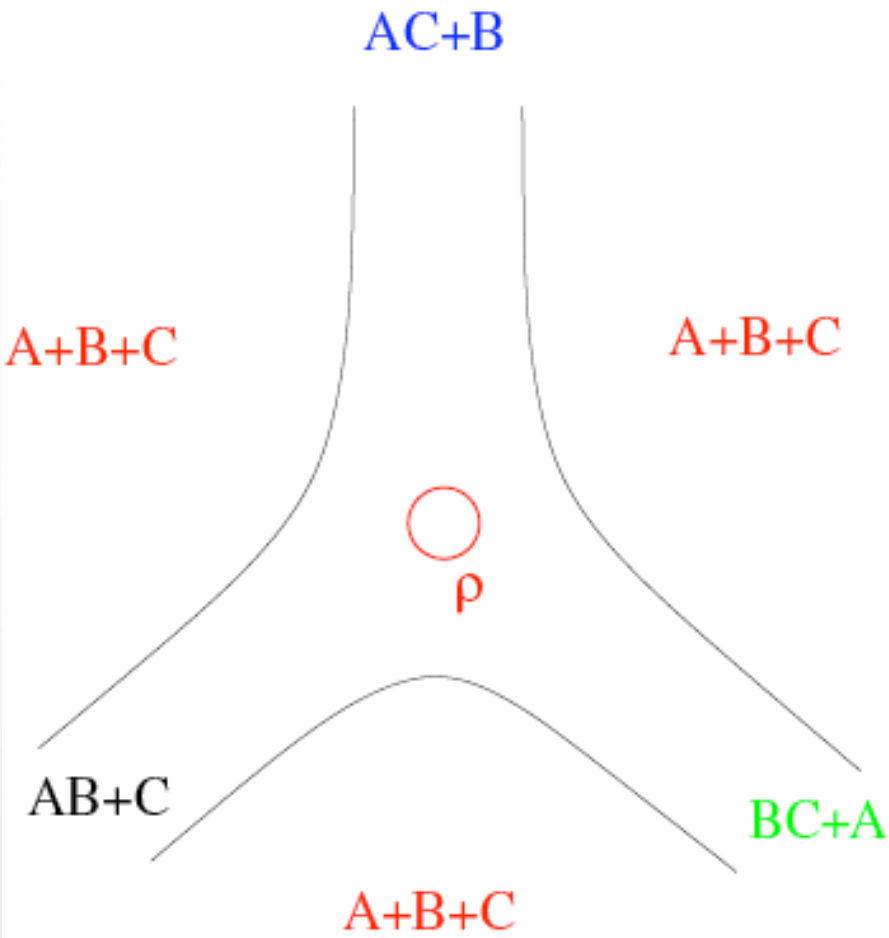
Mass Scaled Jacobi Coordinates

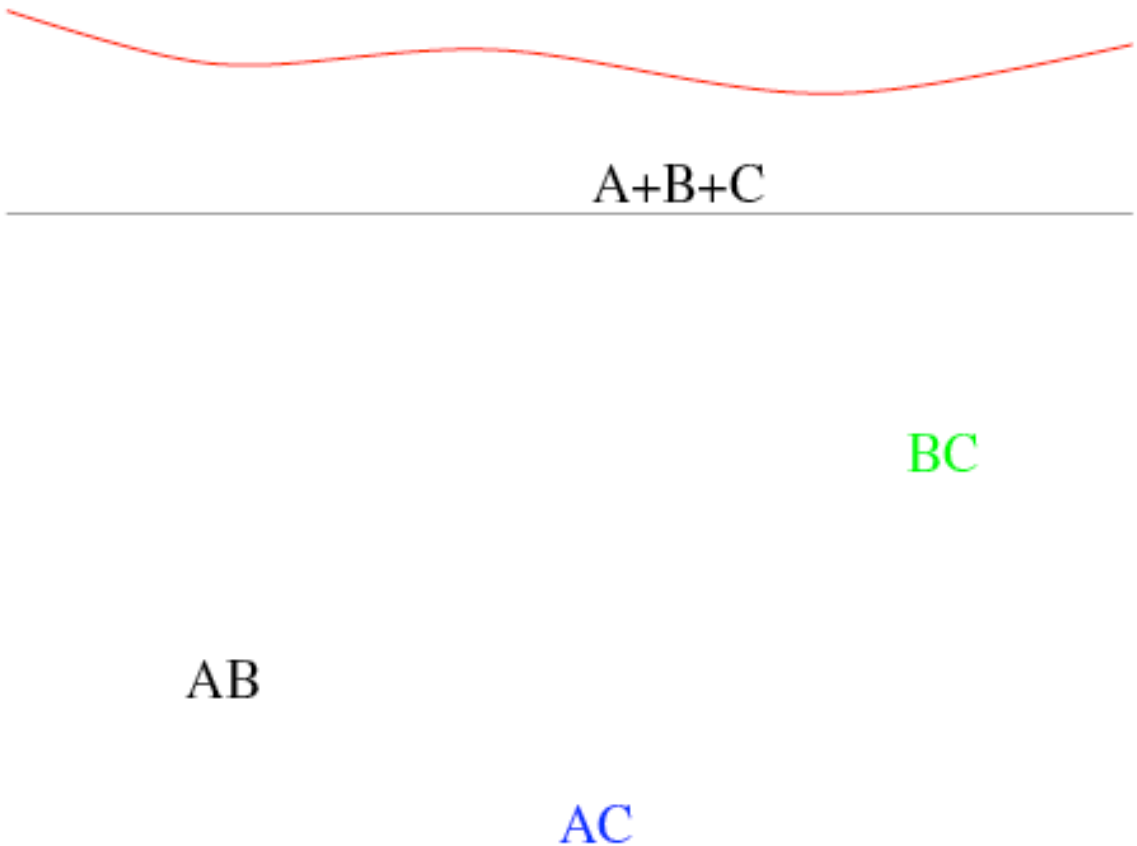
$$\mathbf{S}_\gamma = d_\gamma \mathbf{R}_\gamma, \quad \mathbf{s}_\gamma = d_\gamma^{-1} \mathbf{r}_\gamma$$

Delves Hyperspherical Coordinates ← Scaled Jacobi:

$$\begin{aligned} \rho^2 &= (S_\gamma^2 + s_\gamma^2) \\ \theta_\gamma &= tan^{-1}\left(\frac{s_\gamma}{S_\gamma}\right) \end{aligned}$$

How do the new coordinates work?





Basis:

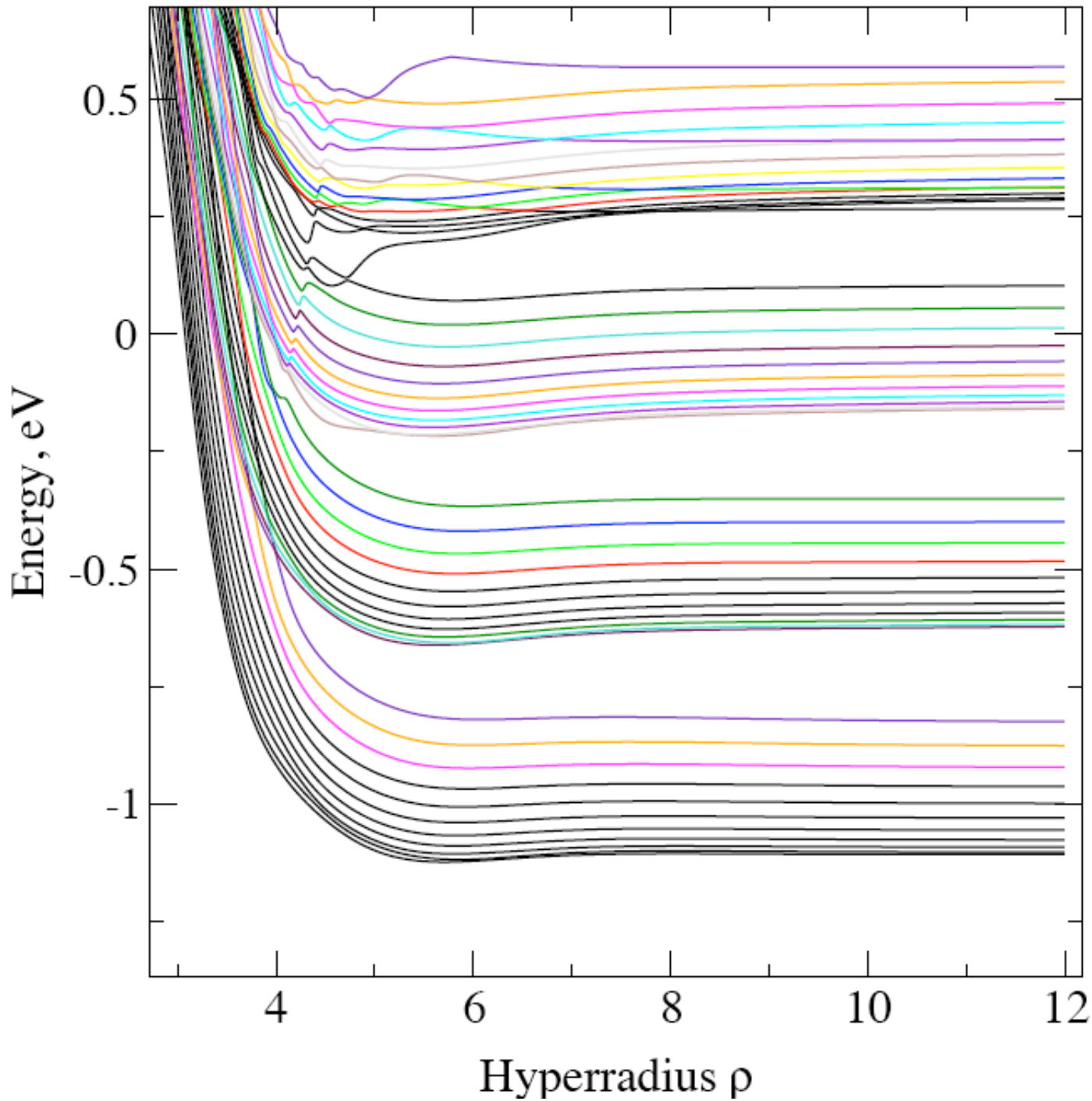
$$\chi_{\alpha v j}(\theta_\alpha;\rho)|jM_j\rangle|\ell M_\ell\rangle = \chi_{\alpha v j}(\theta_\alpha;\rho)Y_{jM_j}(\hat{r}_\alpha)Y_{\ell M_\ell}(\hat{R}_\alpha)$$

where

$$\tilde{H}_{\text{mol}}\,\chi_{\alpha v j}(\theta_\alpha;\rho) = \epsilon_{\alpha v j}(\rho)\chi_{\alpha v j}(\theta_\alpha;\rho)$$

Note that this basis is not orthonormal because the functions of different chemical arrangements overlap. This is taken care of by the transformation:

$$|\zeta_n\rangle = \frac{1}{\sqrt{\lambda_{n\,jM_j,\ell M_\ell}}} \sum X_{\alpha v j M_j \ell M_\ell, n}\chi_{\alpha v j}(\theta_\alpha;\rho)|jM_j\rangle|\ell M_\ell\rangle$$


0.5
0
-0.5
-1
Energy, eV
4
6
8
10
12
Hyperradius ρ

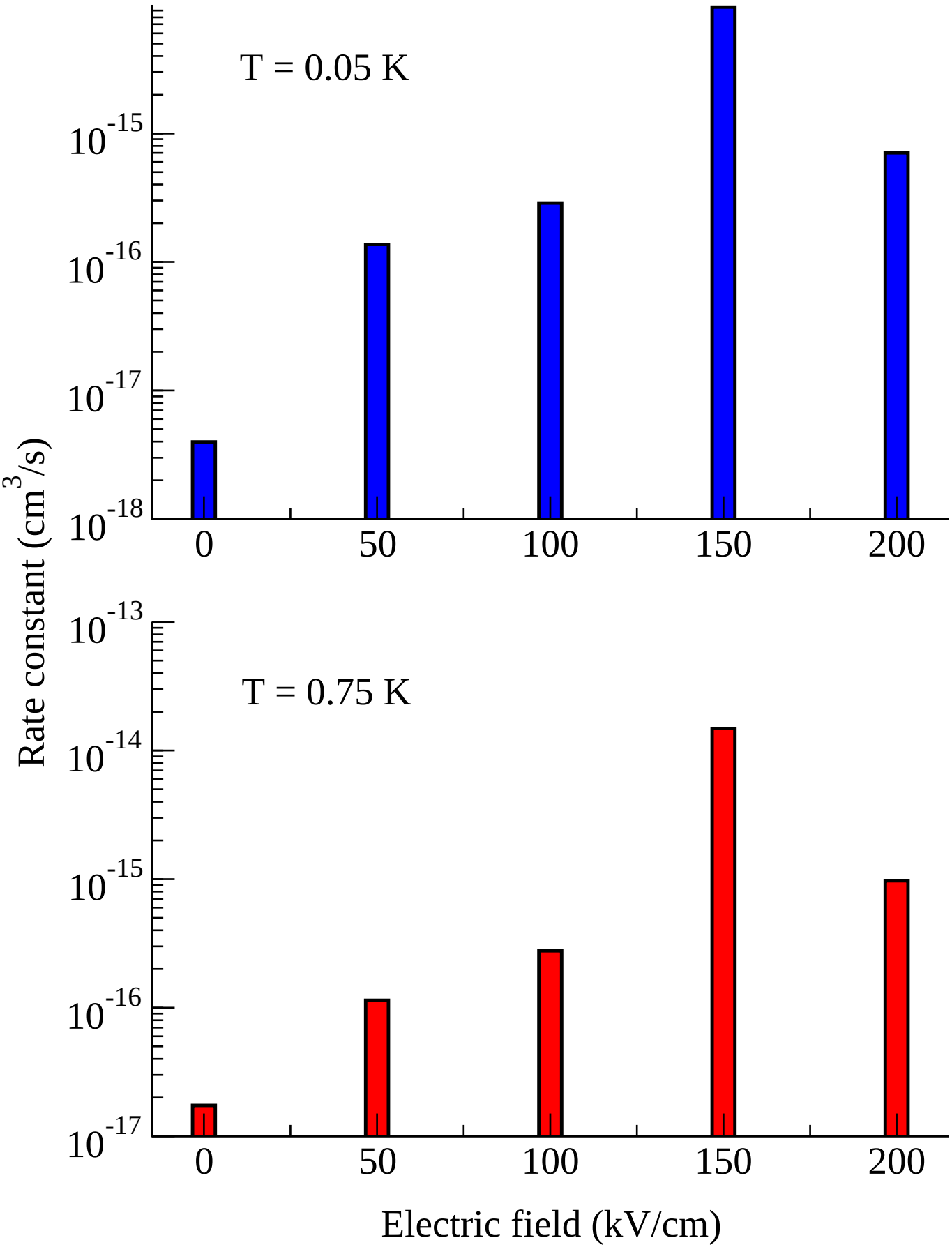
THE JOURNAL OF CHEMICAL PHYSICS **129**, 034112 (2008)

Quantum theory of chemical reactions in the presence of electromagnetic fields

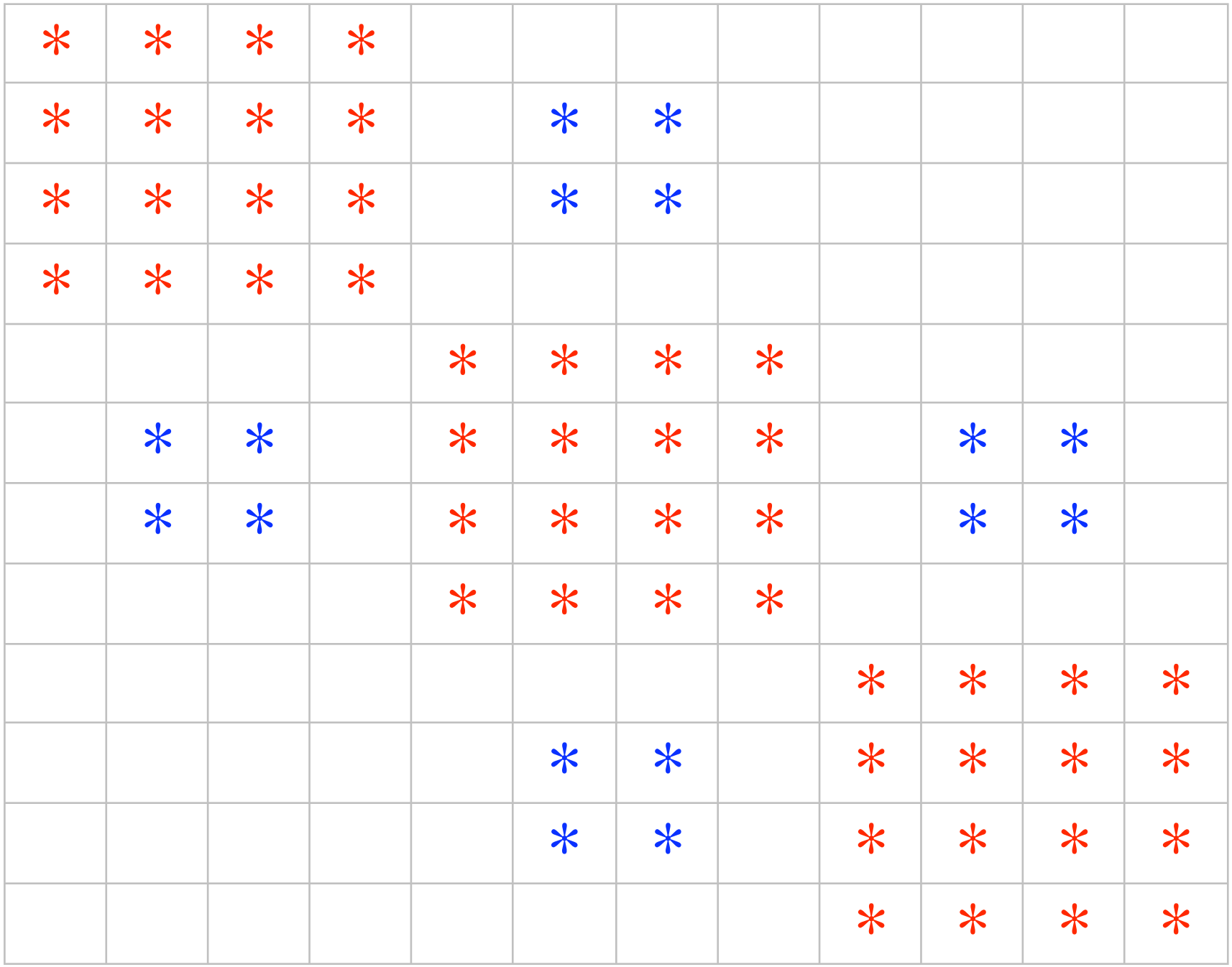
T. V. Tscherbul[a)] and R. V. Krems
Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T 1Z1, Canada

(Received 29 April 2008; accepted 12 June 2008; published online 21 July 2008)

We present a theory for rigorous quantum scattering calculations of probabilities for chemical reactions of atoms with diatomic molecules in the presence of an external electric field. The approach is based on the fully uncoupled basis set representation of the total wave function in the space-fixed coordinate frame, the Fock–Delves hyperspherical coordinates, and the adiabatic partitioning of the total Hamiltonian of the reactive system. The adiabatic channel wave functions


T = 0.05 K
T = 0.75 K
Rate constant (cm3/s)
10-15
10-16
10-17
10-18
10-13
10-14
10-15
10-16
10-17
0
50
100
150
200
Electric field (kV/cm)

Hamiltonian in the presence of an external field



Collisions in laser fields

Polar molecules in a microwave cavity

Molecular Hamiltonian: $H_{\mathrm{mol}} = B\boldsymbol{N}^2$

Field Hamiltonian: $H_{\mathrm{f}} = \hbar\omega(\hat{a}\hat{a}^\dagger - \bar{N})$

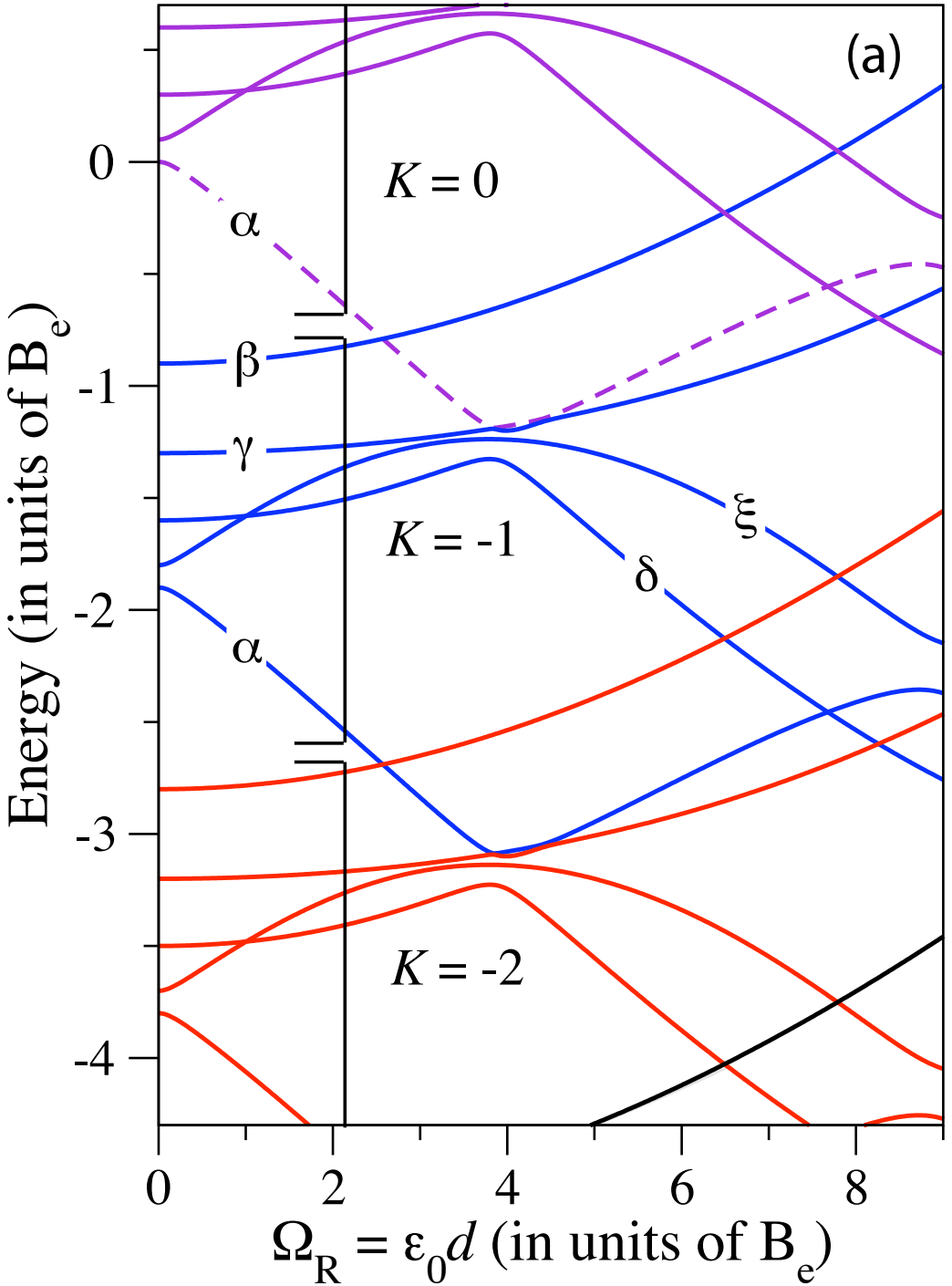
Molecule - Field Interaction: $H_{\mathrm{mol,f}} = -\frac{d\epsilon_0}{2\sqrt{\bar{N}}}\left(\hat{a} + \hat{a}^\dagger\right)\cos\chi$

Basis set: $|NM_N\rangle|\bar{N}+n\rangle$

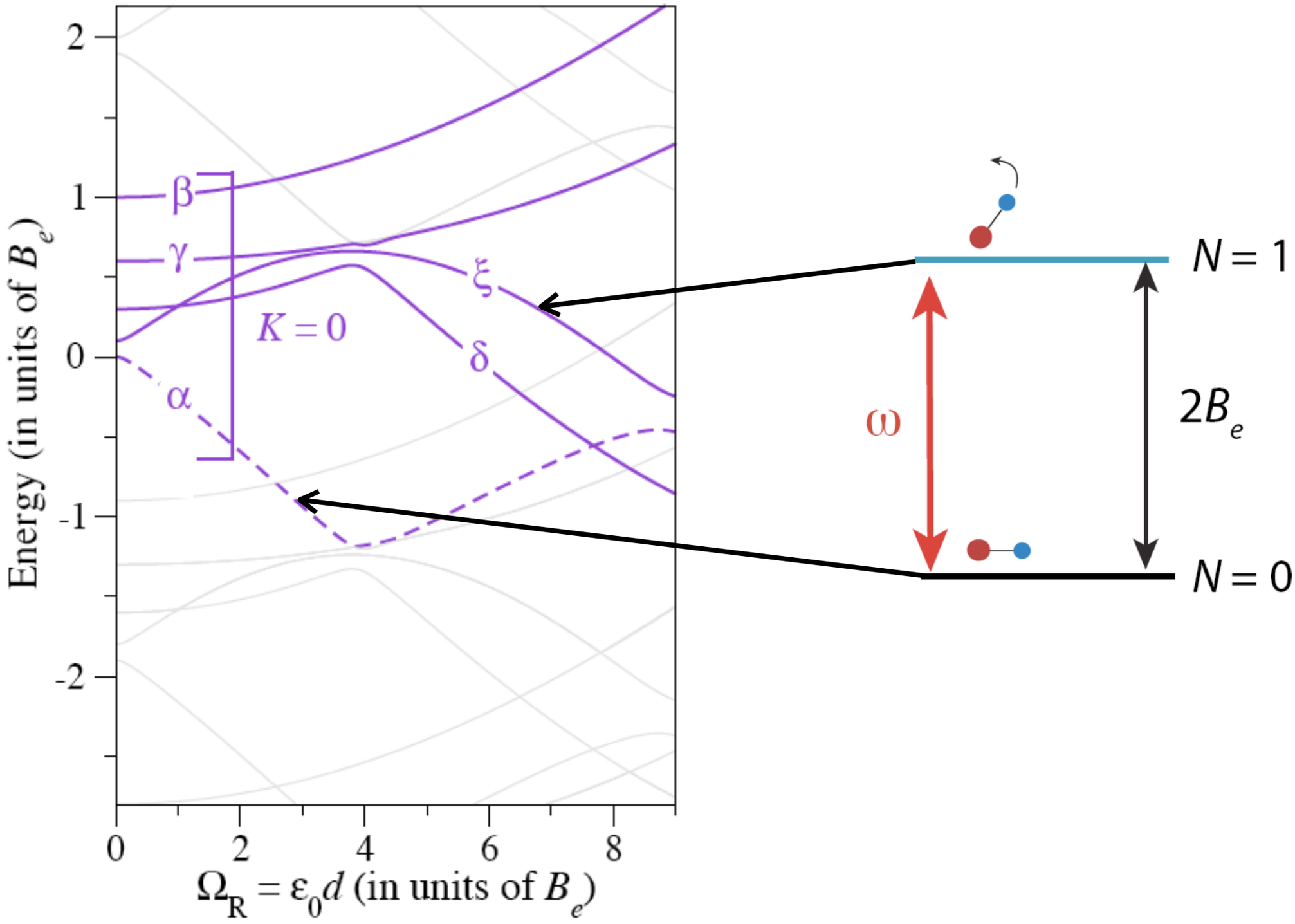
The matrix elements:

$$\langle\bar{N}+n|\langle NM_N|H_{\mathrm{mol,f}}|N'M'_N\rangle|\bar{N}+n'\rangle \sim \langle NM_N|\cos\chi|N'M'_N\rangle \times \times\left(\delta_{n,n'+1} + \delta_{n,n'-1}\right)$$

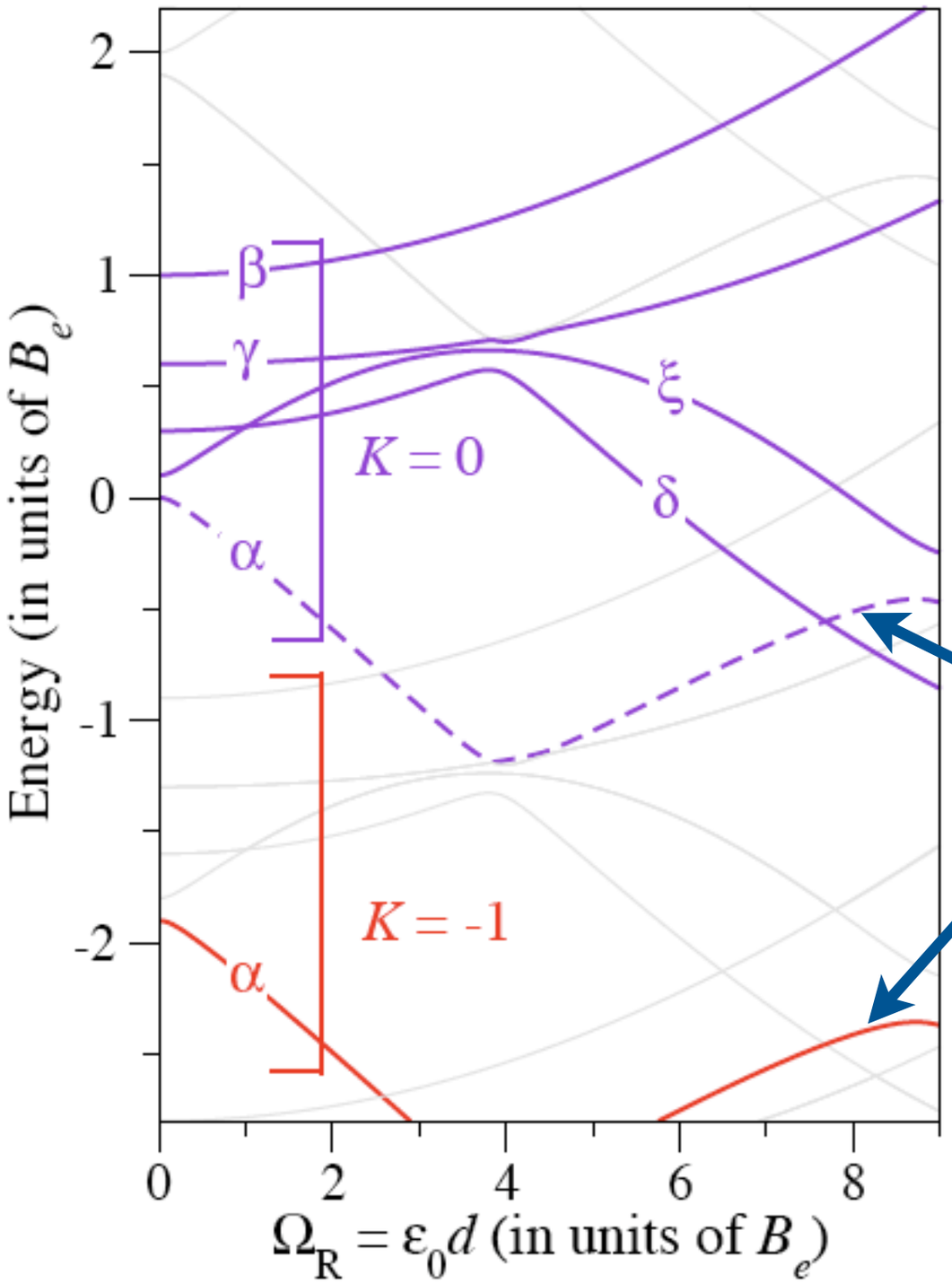
$$\langle NM_N|\cos\chi|N'M'_N\rangle \sim \delta_{M_N,M'_N}\left(\delta_{N,N'+1} + \delta_{N,N'-1}\right)$$

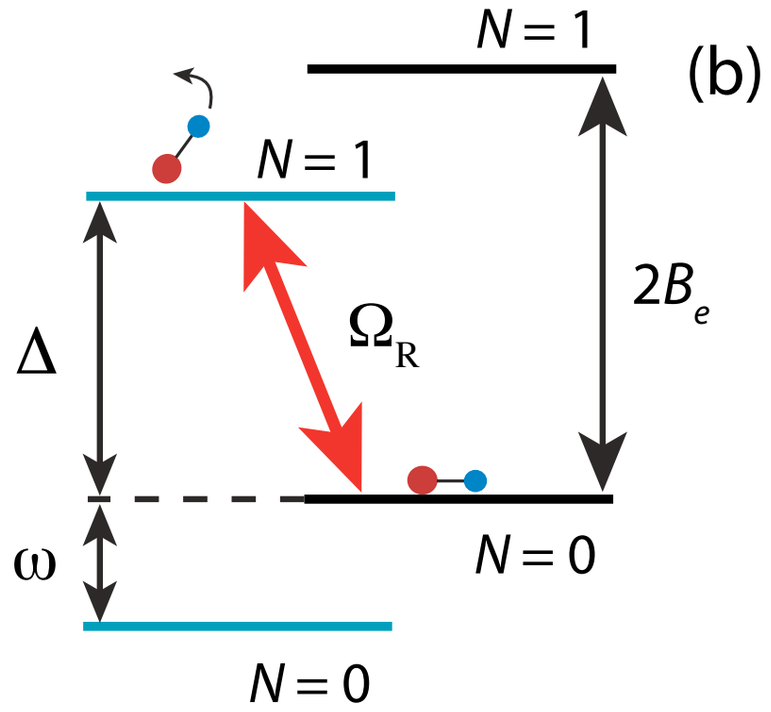

(a)
K = 0
K = -1
K = -2
α
β
γ
δ
ξ
α
0
-1
-2
-3
-4
0
2
4
6
8
Energy (in units of B_e)
Ω_R = ε_0 d (in units of B_e)

Polar molecule in a microwave cavity



Polar molecule in a microwave cavity

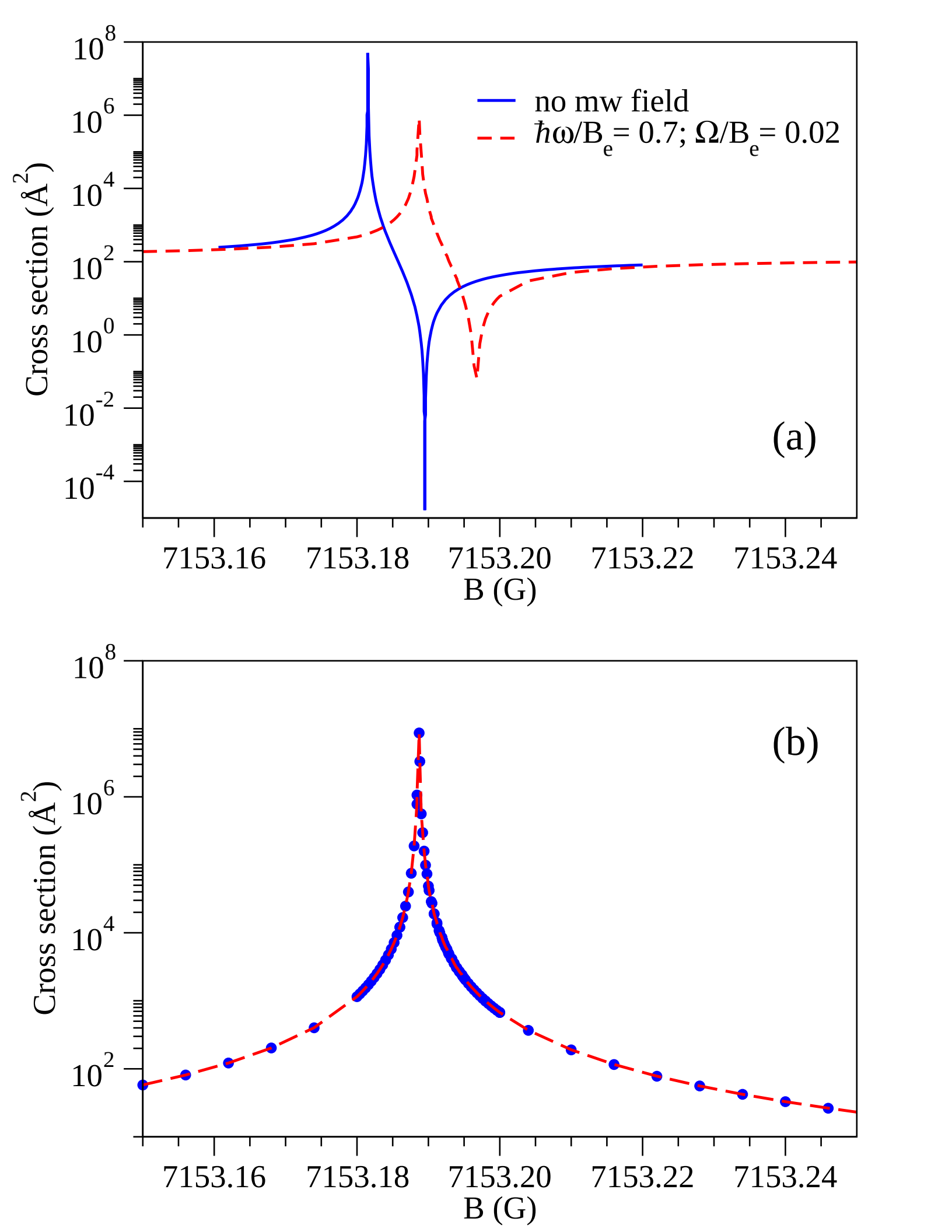




$$a_0|N=0,\bar{N}\rangle + a_1|N=1,\bar{N}-1\rangle$$

$$a_0|N=0,\bar{N}-1\rangle + a_1|N=1,\bar{N}-2\rangle$$

- no absolute ground state


no mw field
ħω/B_e = 0.7; Ω/B_e = 0.02
Cross section (Å^2)
B (G)
(a)
(b)
10^8
10^6
10^4
10^2
10^0
10^-2
10^-4
7153.16
7153.18
7153.20
7153.22
7153.24

Challenges for theory of molecular collisions in external fields

Large basis sets = need decoupling approximations

Lack of accurate intermolecular potentials = need experimental data

Lack of rigorous theories connecting short-range interaction physics and long-range dynamics

Is there universality in molecular collisions at finite temperature?