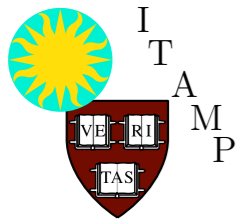


A perturbed Rydberg atom

H. R. Sadeghpour
ITAMP, Harvard-Smithsonian Center for Astrophysics

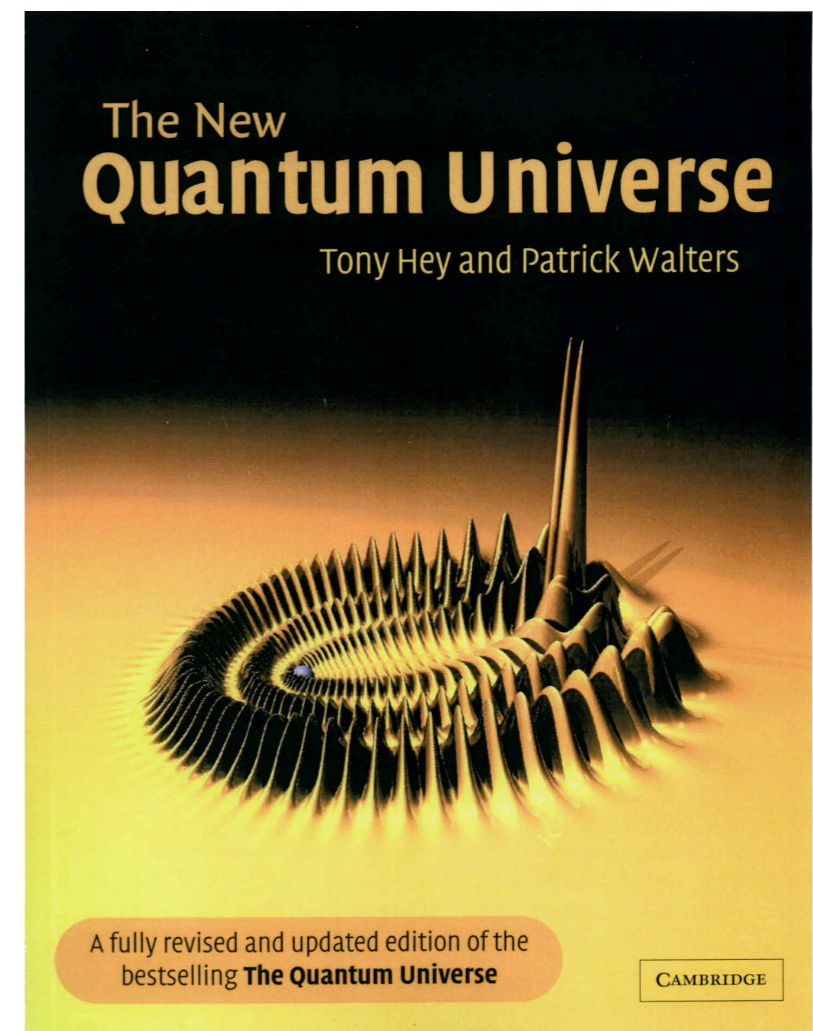
“This book will amaze, baffle and delight ...” - Nature



A perturbed Rydberg atom

H. R. Sadeghpour
ITAMP, Harvard-Smithsonian Center for Astrophysics

“This book will amaze, baffle and delight ...” - Nature



Baranger ... (1958)

Impact approximation...

Baranger ... (1958)

strong (but) binary interactions ...

Impact approximation...

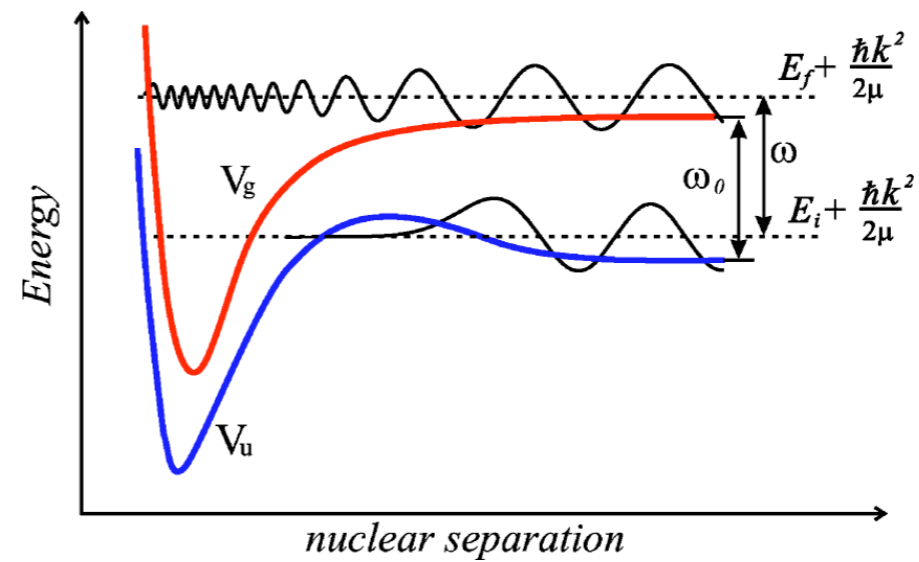
Baranger ... (1958)

strong (but) binary interactions ...

$$I(\omega) \sim \frac{|\langle \beta | e \mathbf{r} | \alpha \rangle|^2}{(\omega - \omega_0 - d)^2 + (\Gamma/2 + w)^2}$$

↗ shift
↘ width

$$w - id \equiv \Delta_{\beta\alpha} = \hbar n \langle v \sigma_{\beta\alpha} \rangle = p \frac{\hbar \langle v \rangle}{k_B T} \langle \sigma_{\beta\alpha} \rangle$$



Impact approximation...

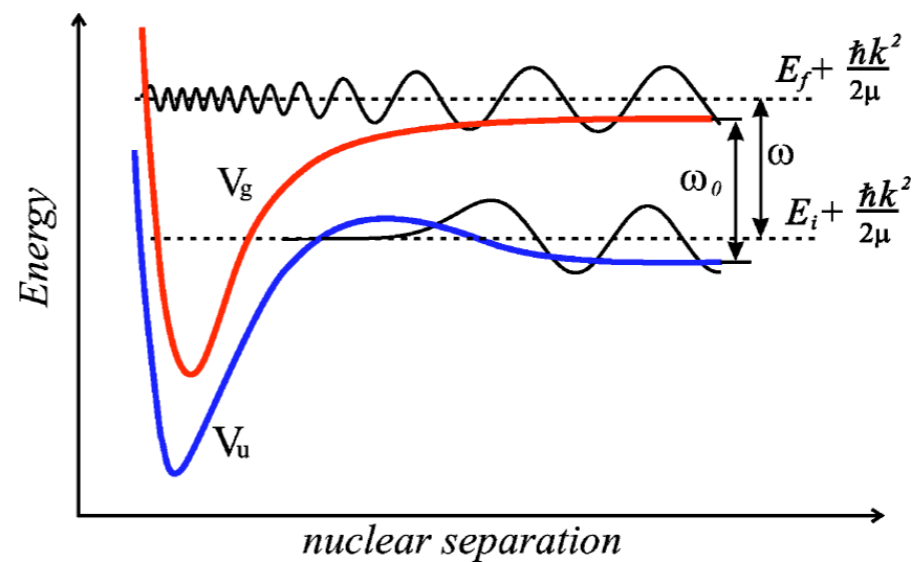
Baranger ... (1958)

strong (but) binary interactions ...

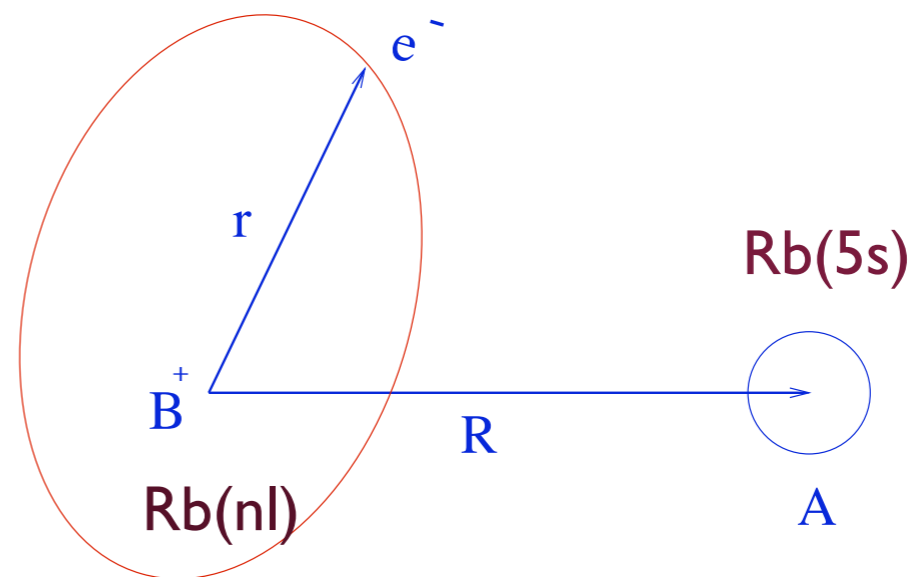
$$I(\omega) \sim \frac{|\langle \beta | e \mathbf{r} | \alpha \rangle|^2}{(\omega - \omega_0 - d)^2 + (\Gamma/2 + w)^2}$$

↖ shift
↗ width

$$w - id \equiv \Delta_{\beta\alpha} = \hbar n \langle v \sigma_{\beta\alpha} \rangle = p \frac{\hbar \langle v \rangle}{k_B T} \langle \sigma_{\beta\alpha} \rangle$$



$$V(\mathbf{R}, \mathbf{r}) = V_{e-A}(\mathbf{R}, \mathbf{r}) + V_{pol}(\mathbf{R}, \mathbf{r})$$



Impact approximation...

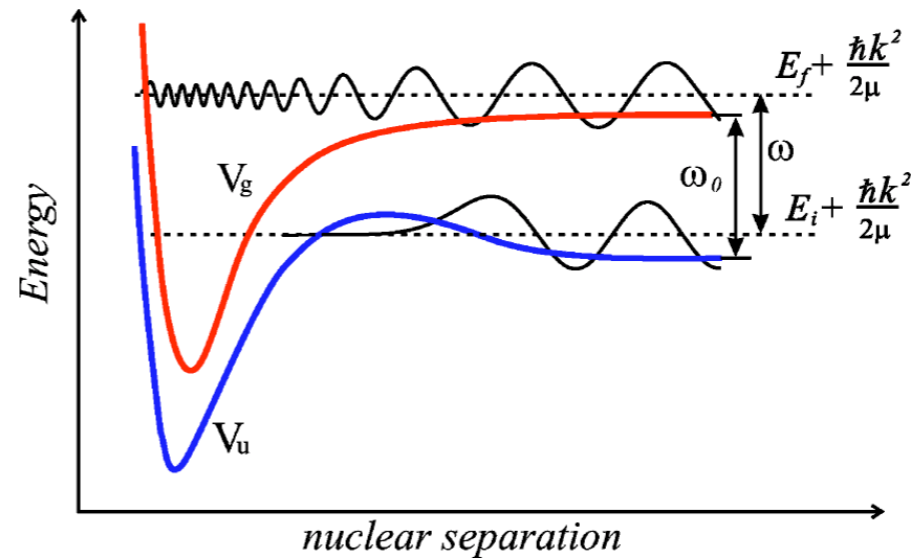
Baranger ... (1958)

strong (but) binary interactions ...

$$I(\omega) \sim \frac{|\langle \beta | e \mathbf{r} | \alpha \rangle|^2}{(\omega - \omega_0 - d)^2 + (\Gamma/2 + w)^2}$$

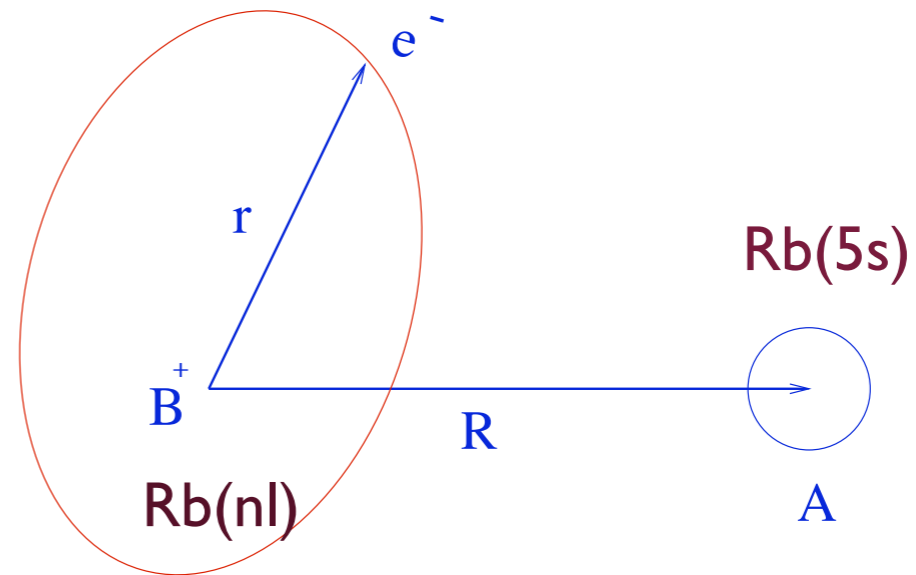
↖ shift
↗ width

$$w - id \equiv \Delta_{\beta\alpha} = \hbar n \langle v \sigma_{\beta\alpha} \rangle = p \frac{\hbar \langle v \rangle}{k_B T} \langle \sigma_{\beta\alpha} \rangle$$



$$V(\mathbf{R}, \mathbf{r}) = V_{e-A}(\mathbf{R}, \mathbf{r}) + V_{pol}(\mathbf{R}, \mathbf{r})$$

$$V_{pol}(\mathbf{R}, \mathbf{r}) = -\frac{\alpha}{2R^4} + \alpha \frac{R^2 - (\mathbf{R} \cdot \mathbf{r})}{R^3 |\mathbf{R} - \mathbf{r}|^3} - \frac{\alpha}{2|\mathbf{R} - \mathbf{r}|^4}$$

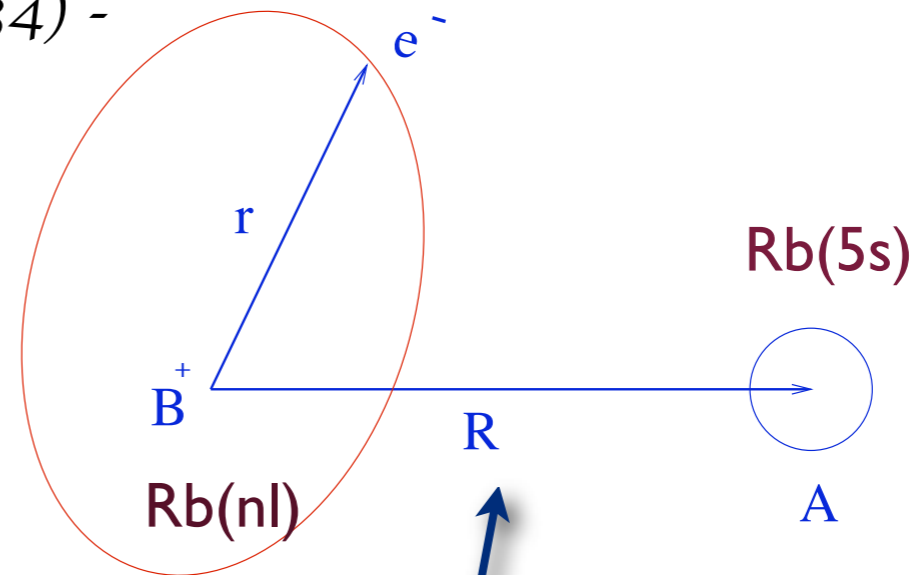


$$V_{e-A}(\mathbf{R}, \mathbf{r}) = V_0 \delta(\mathbf{r} - \mathbf{R}) - \frac{\alpha_A}{2|\mathbf{r} - \mathbf{R}|^4}$$

Fermi pseudopotential

Fermi observed that how Rydberg lines shifted depended on the species.... species-dependent scattering length

*Contact interaction (Nuovo Cimento 11, 157(1934) -
pressure broadening and shift*



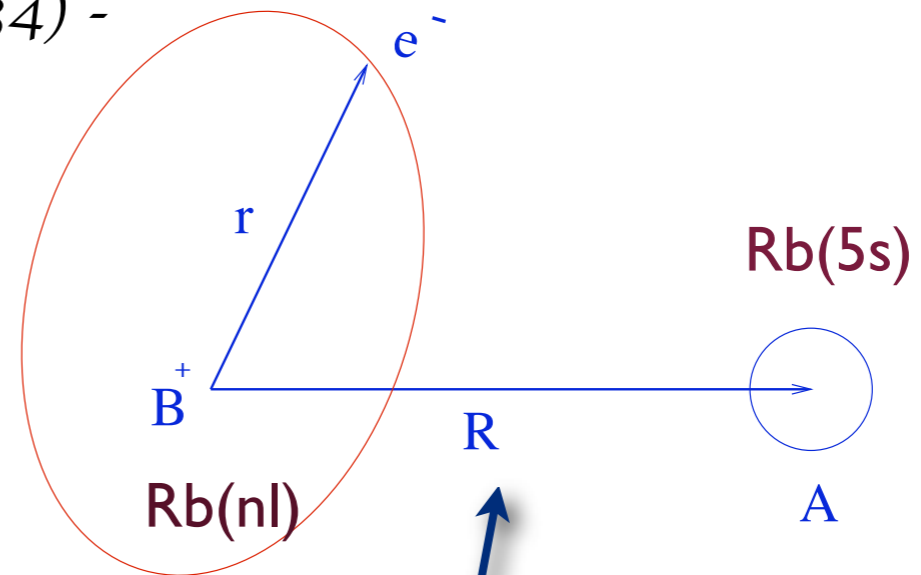
$$V_{pol}(R) = -\frac{\alpha_A}{2R^4}$$

Fermi pseudopotential

Fermi observed that how Rydberg lines shifted depended on the species.... species-dependent scattering length

*Contact interaction (Nuovo Cimento 11, 157(1934) -
pressure broadening and shift*

$$V_{e^-A}(\mathbf{r}, \mathbf{R}) = V_0 \delta(\mathbf{r} - \mathbf{R}) = 2\pi a_T [k(R)] \delta(\mathbf{r} - \mathbf{R})$$



$$V_{pol}(R) = -\frac{\alpha_A}{2R^4}$$

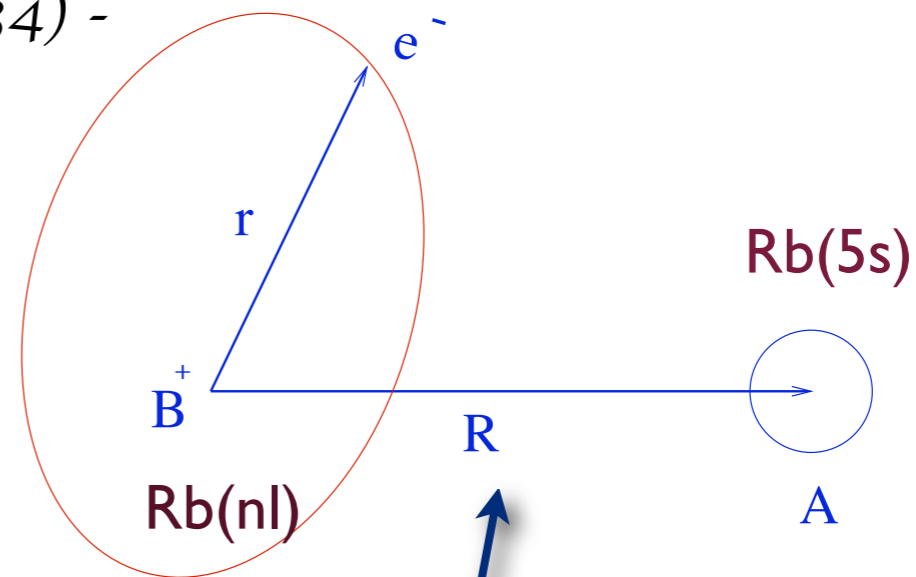
Fermi pseudopotential

Fermi observed that how Rydberg lines shifted depended on the species.... species-dependent scattering length

Contact interaction (Nuovo Cimento 11, 157(1934) - pressure broadening and shift

$$V_{e^-A}(\mathbf{r}, \mathbf{R}) = V_0 \delta(\mathbf{r} - \mathbf{R}) = 2\pi a_T [k(R)] \delta(\mathbf{r} - \mathbf{R})$$

$$\frac{1}{2}k^2(R) = -\frac{1}{2n^2} + \frac{1}{R}$$



$$V_{pol}(R) = -\frac{\alpha_A}{2R^4}$$

Fermi pseudopotential

Fermi observed that how Rydberg lines shifted depended on the species.... species-dependent scattering length

Contact interaction (Nuovo Cimento 11, 157(1934) - pressure broadening and shift

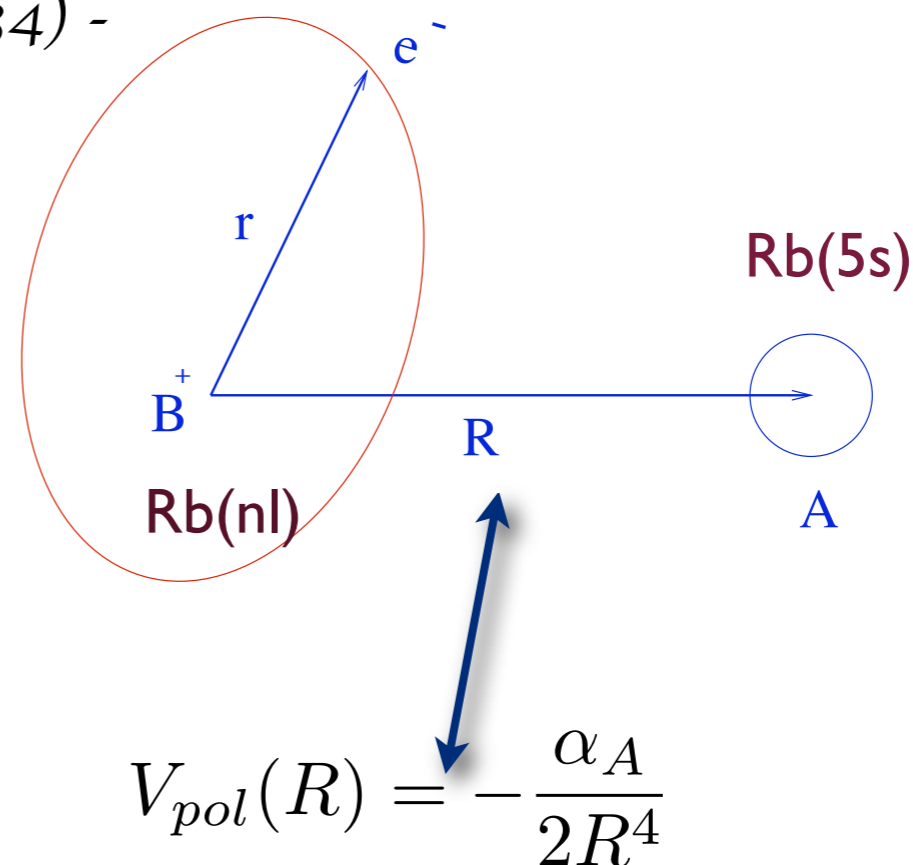
$$V_{e^- - A}(\mathbf{r}, \mathbf{R}) = V_0 \delta(\mathbf{r} - \mathbf{R}) = 2\pi a_T [k(R)] \delta(\mathbf{r} - \mathbf{R})$$

$$\frac{1}{2}k^2(R) = -\frac{1}{2n^2} + \frac{1}{R}$$

$$U(R) = 2\pi \frac{\hbar^2}{m} a |\Psi(\mathbf{R})|^2$$

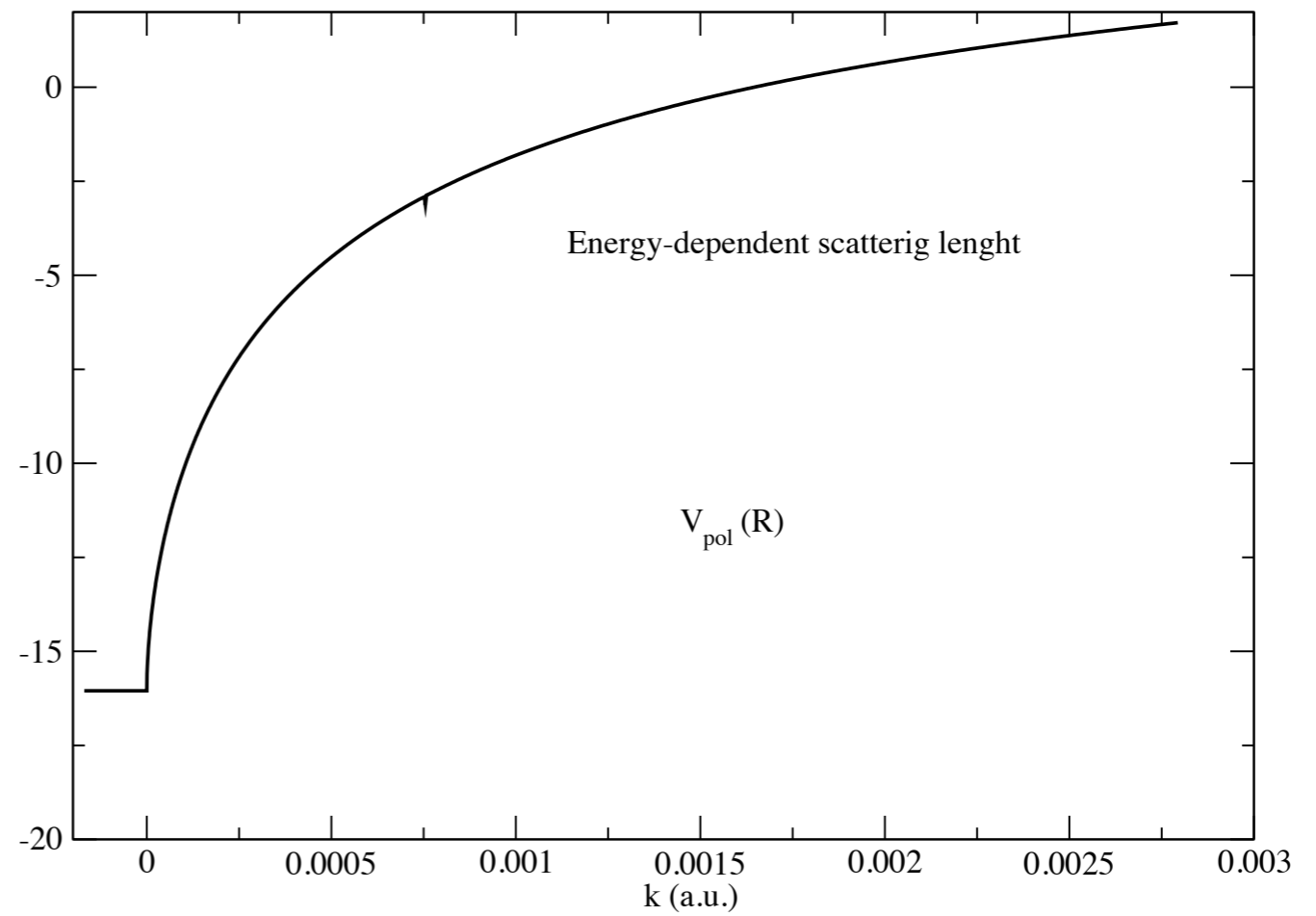
$$a_T[k] = -\tan \delta_0^T(k)/k$$

zero-range e^- scattering leads to long-range molecular binding



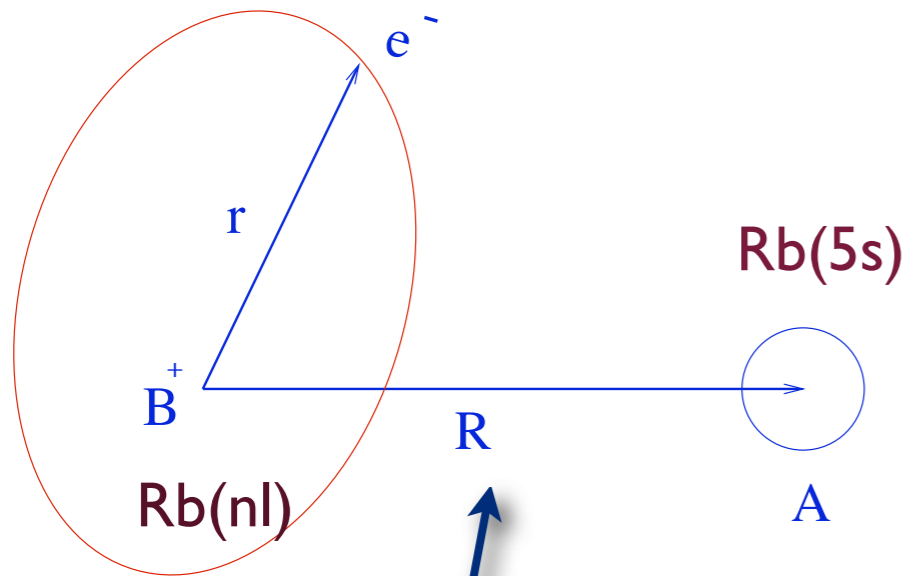
$$V_{pol}(R) = -\frac{\alpha_A}{2R^4}$$

Energy-dependent scattering length

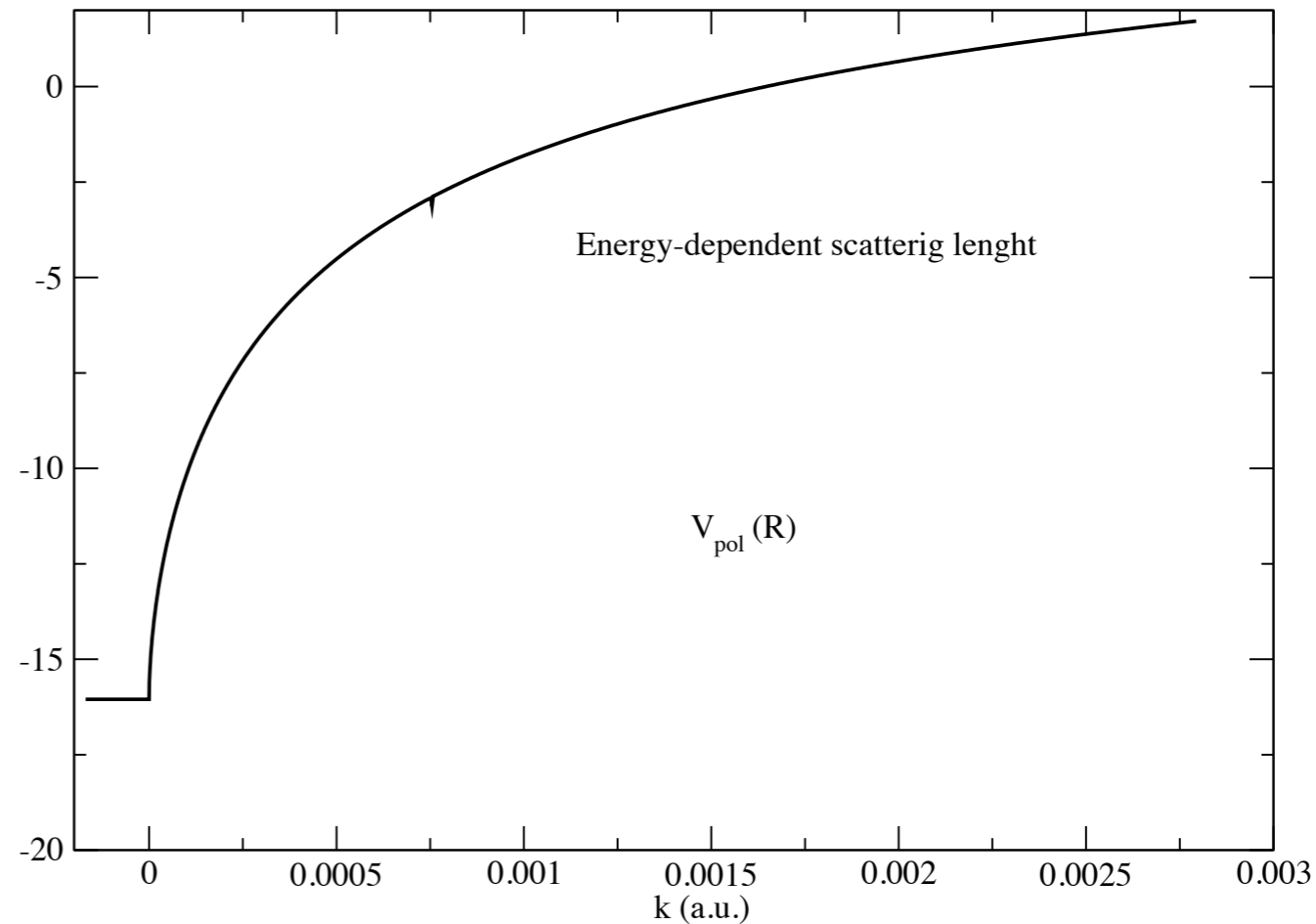


Energy-dependent scattering length

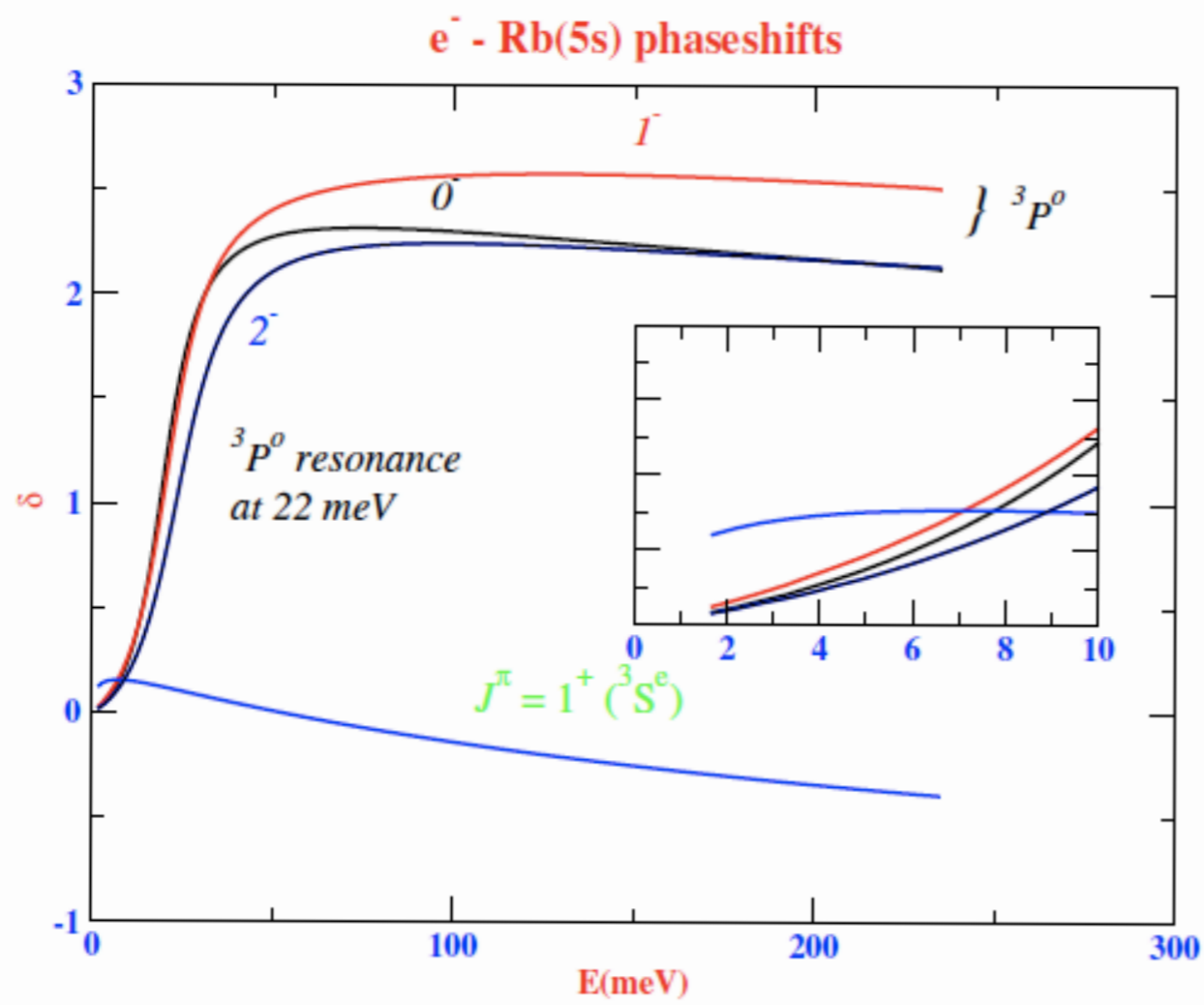
$$V_{e^-A}(\mathbf{r}, \mathbf{R}) = V_0 \delta(\mathbf{r} - \mathbf{R}) = 2\pi a_T[k(R)] \delta(\mathbf{r} - \mathbf{R})$$



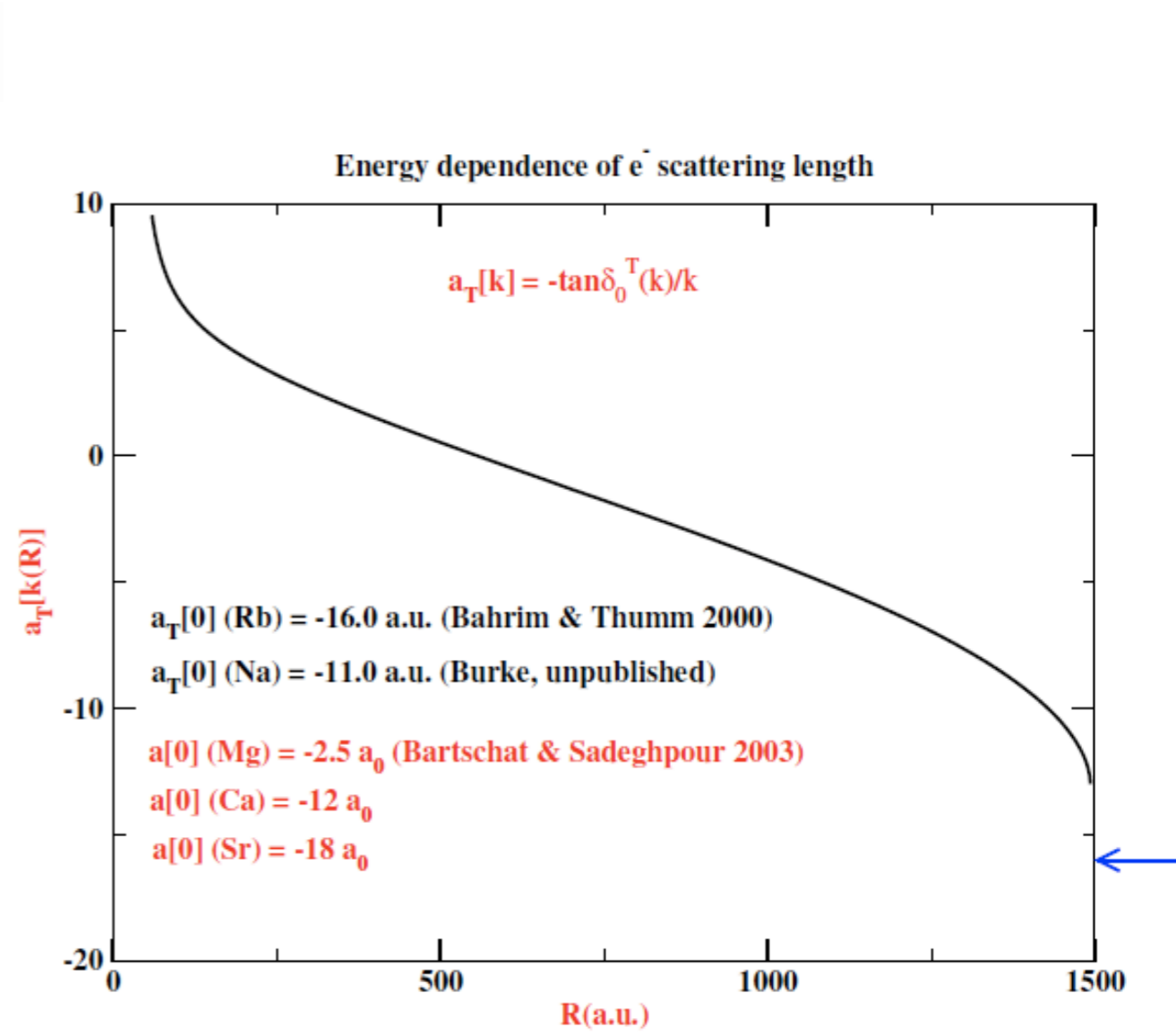
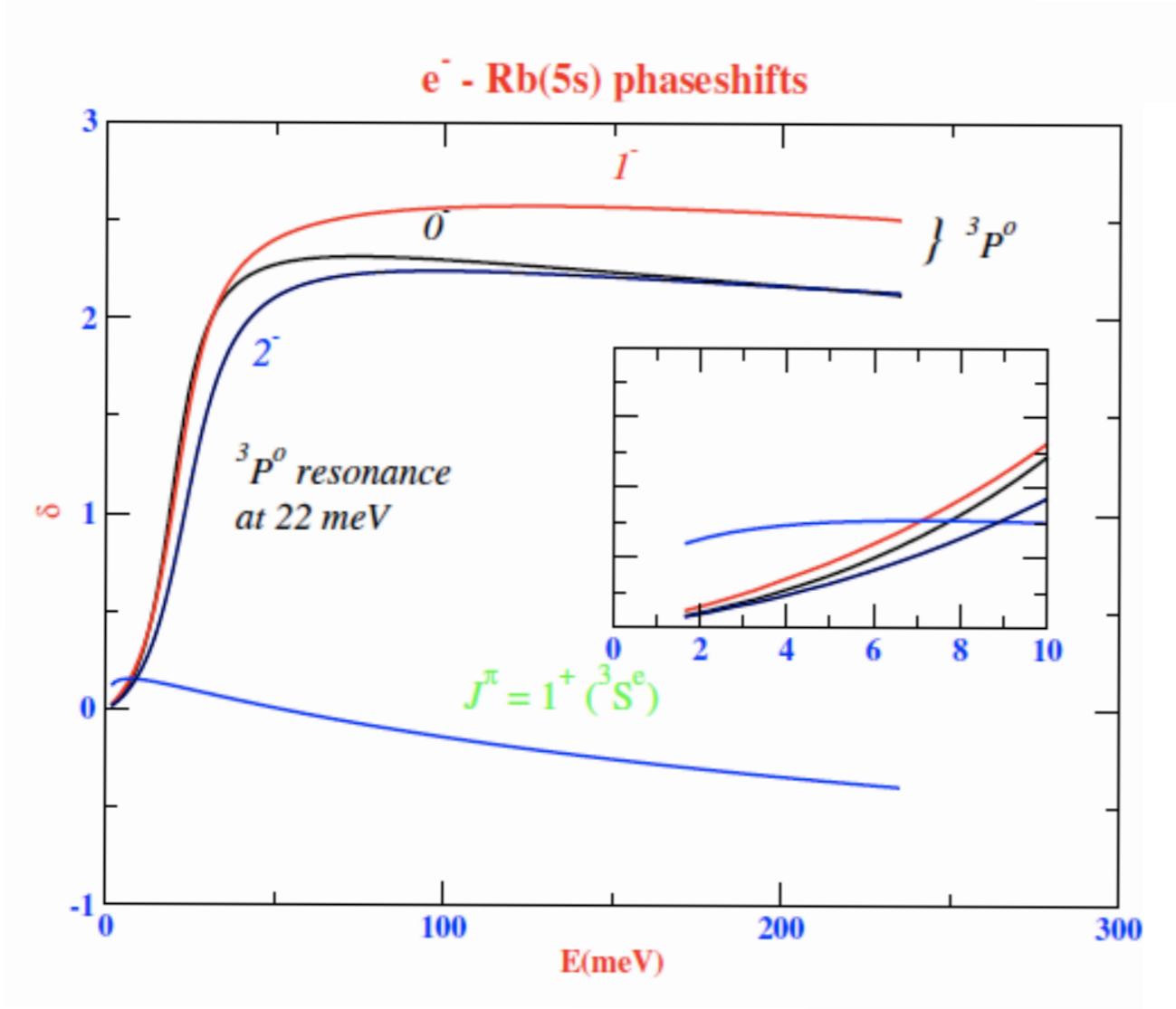
$$V_{pol}(R) = -\frac{\alpha_A}{2R^4}$$



scattering phase shifts

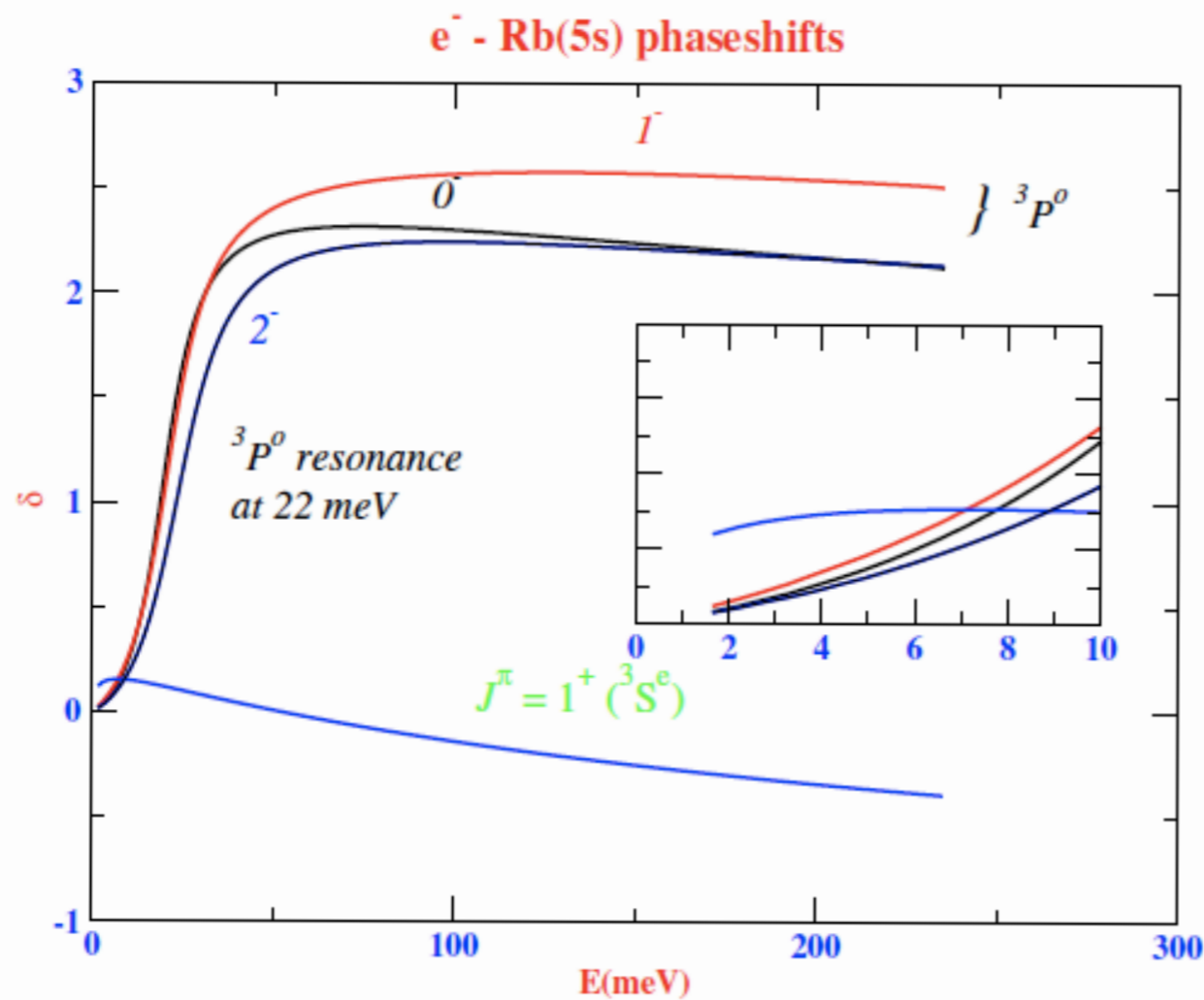


scattering phase shifts



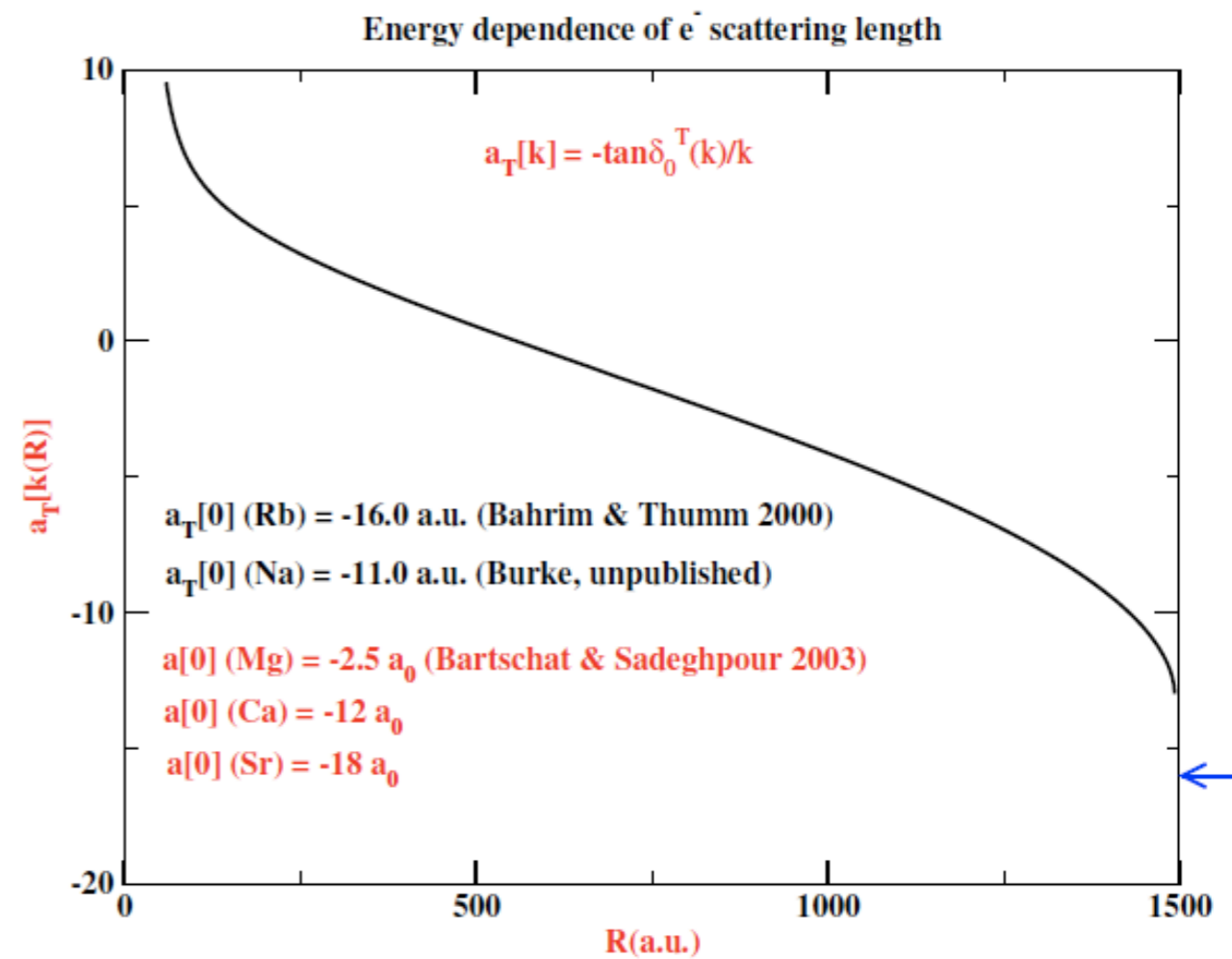
$$V_{e^- - A}(\mathbf{r}, \mathbf{R}) = V_0 \delta(\mathbf{r} - \mathbf{R})$$

scattering phase shifts



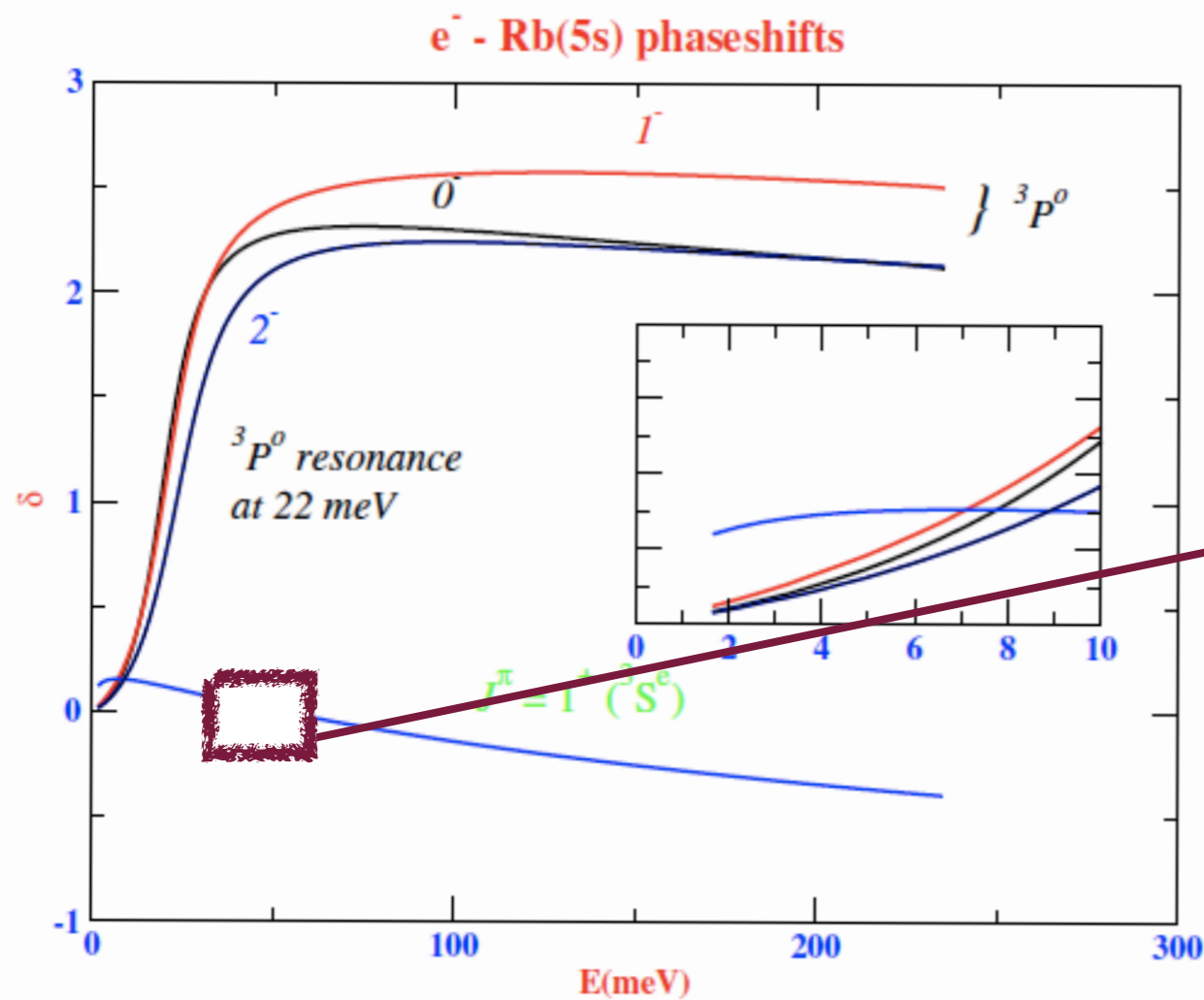
Alkali metals in 3S_e : scattering length --- all negative; form molecular Rydberg levels

Alkali metals in 1S_e : scattering length --- all positive; $a_T(\text{Rb}) = 0.2 a_0$



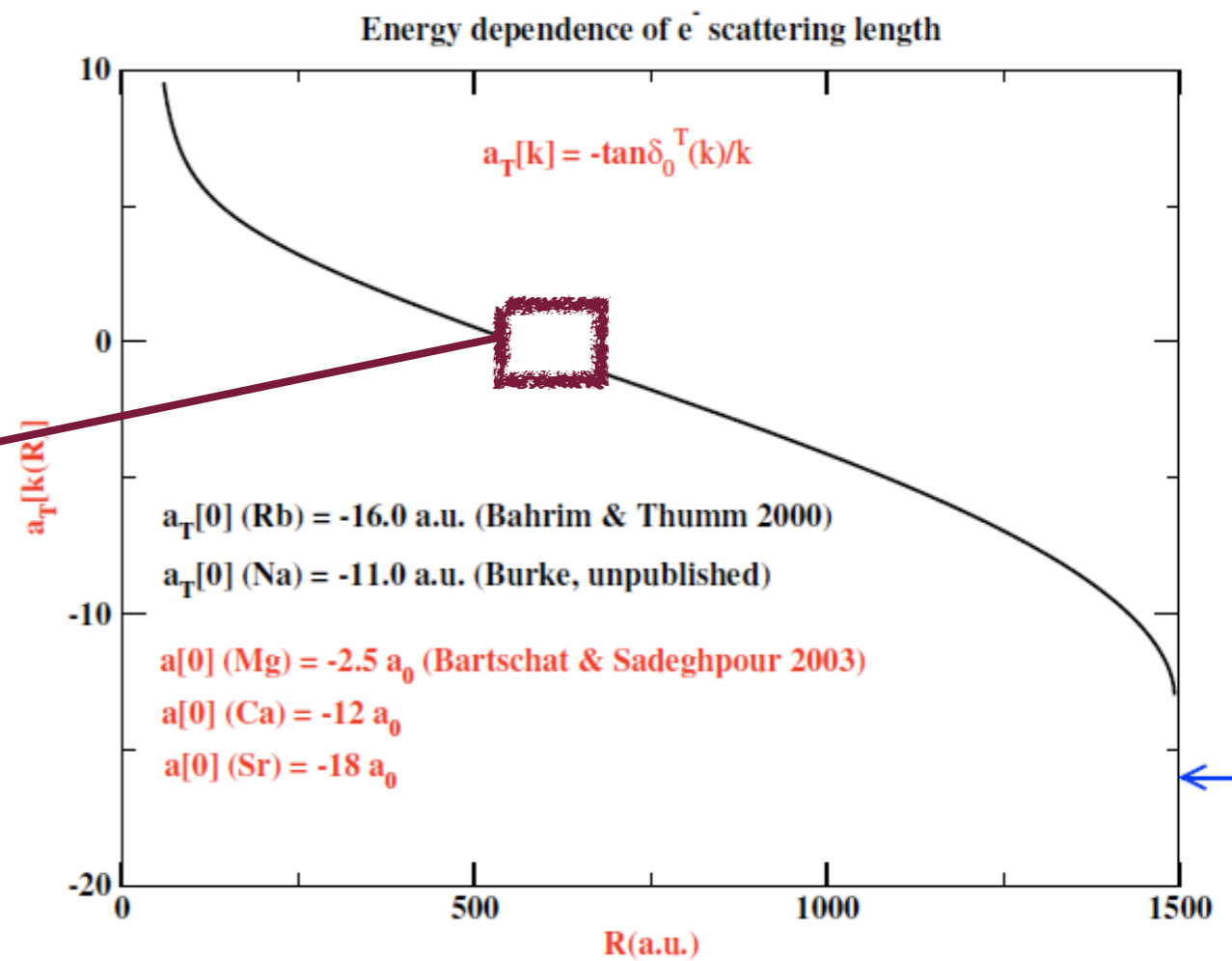
$$V_{e^- - A}(\mathbf{r}, \mathbf{R}) = V_0 \delta(\mathbf{r} - \mathbf{R})$$

scattering phase shifts



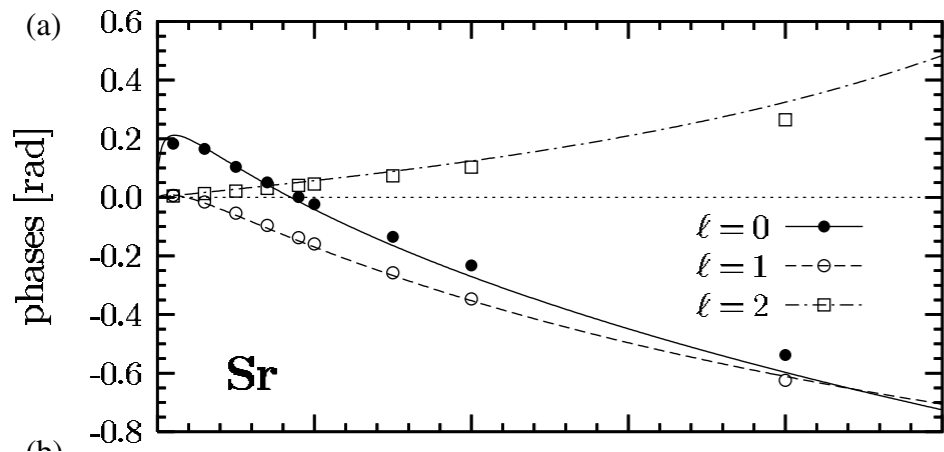
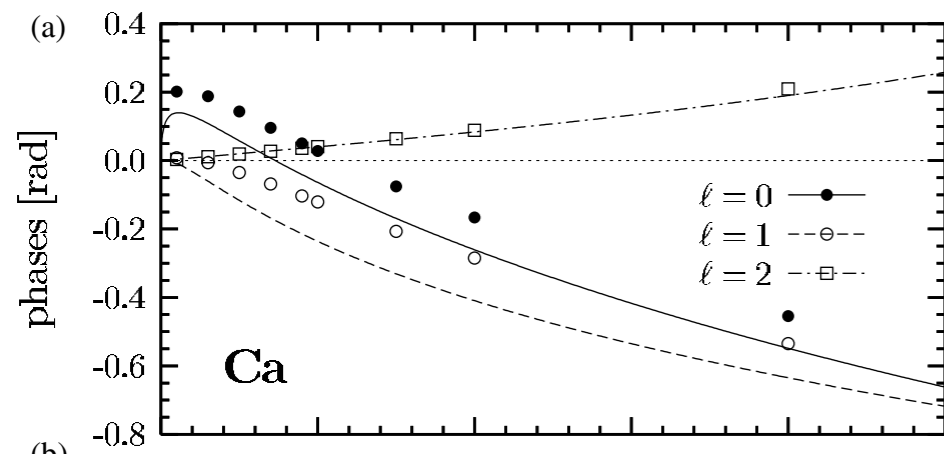
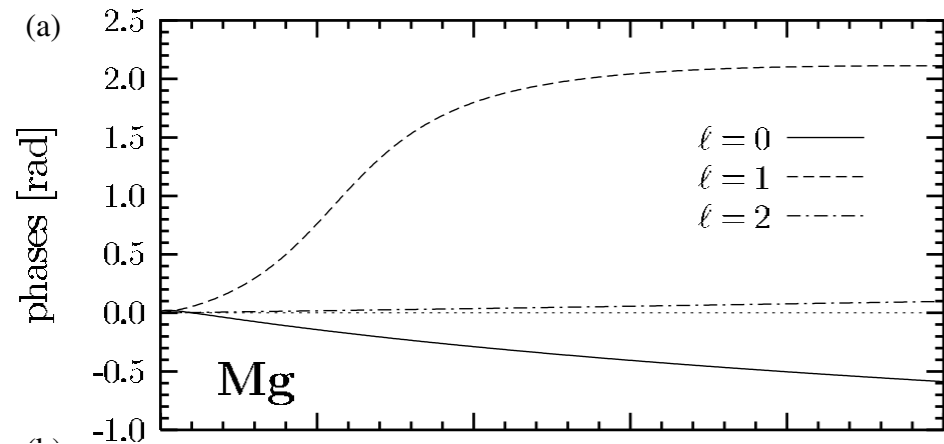
Alkali metals in 3S_e : scattering length --- all negative; form molecular Rydberg levels

Alkali metals in 1S_e : scattering length --- all positive; $a_T(\text{Rb}) = 0.2 a_0$



$$V_{e^- - A}(\mathbf{r}, \mathbf{R}) = V_0 \delta(\mathbf{r} - \mathbf{R})$$

e^- - Alkaline-earth (^{1}Se) elastic phase shift



$$a[0] (\text{Mg}) = -2.5 a_0$$

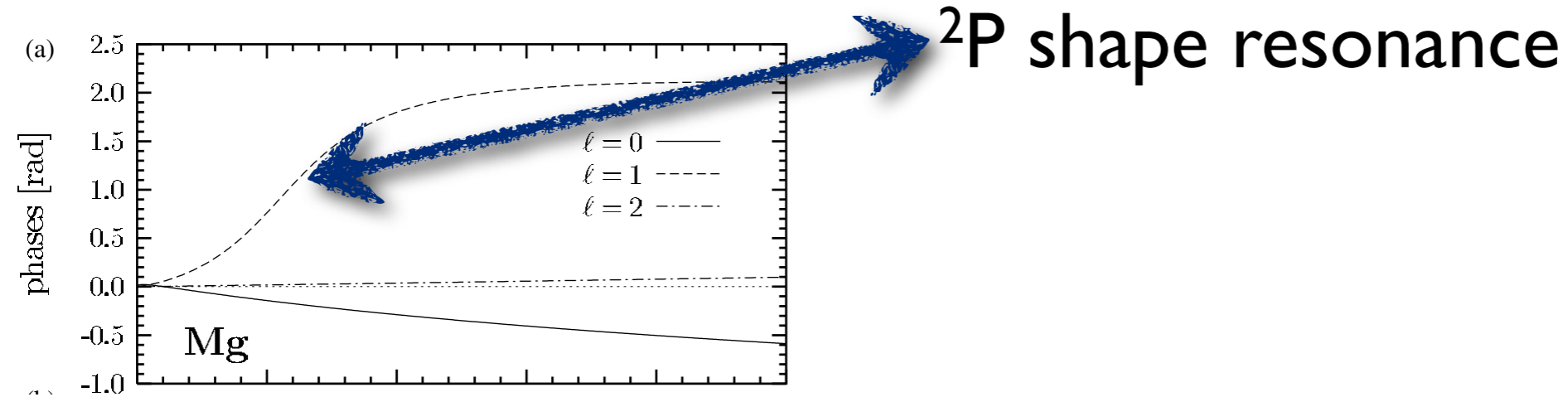
$$a[0] (\text{Ca}) = -12 a_0$$

$$a[0] (\text{Sr}) = -18 a_0$$

R-matrix calculations

Bartschat + Sadeghpour (2003)

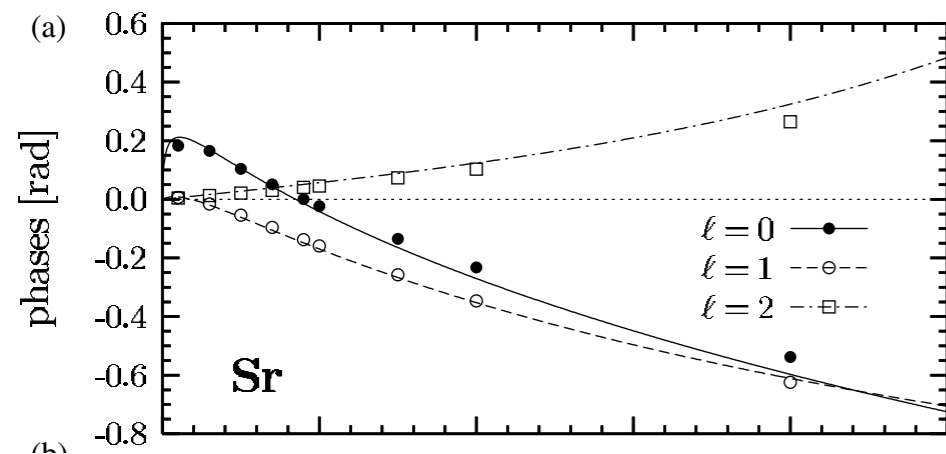
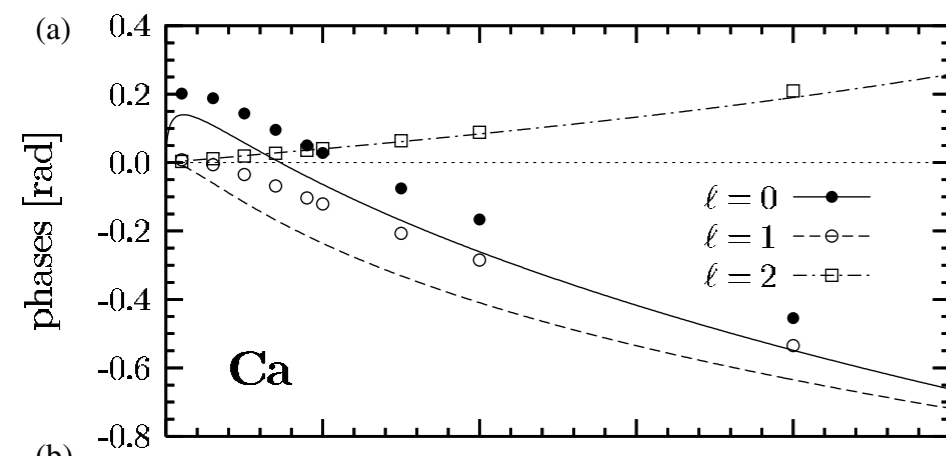
e^- - Alkaline-earth (^{1}Se) elastic phase shift



$a[0] (\text{Mg}) = -2.5 a_0$

$a[0] (\text{Ca}) = -12 a_0$

$a[0] (\text{Sr}) = -18 a_0$



R-matrix calculations

Bartschat + Sadeghpour (2003)

s-wave e⁻ scattering

p-wave e⁻ scattering

$${}^3\Sigma \quad {}^3\Sigma \quad {}^3\Pi$$

Born-Oppenheimer Rydberg molecular potentials

s-wave e⁻ scattering



p-wave e⁻ scattering



Born-Oppenheimer Rydberg molecular potentials

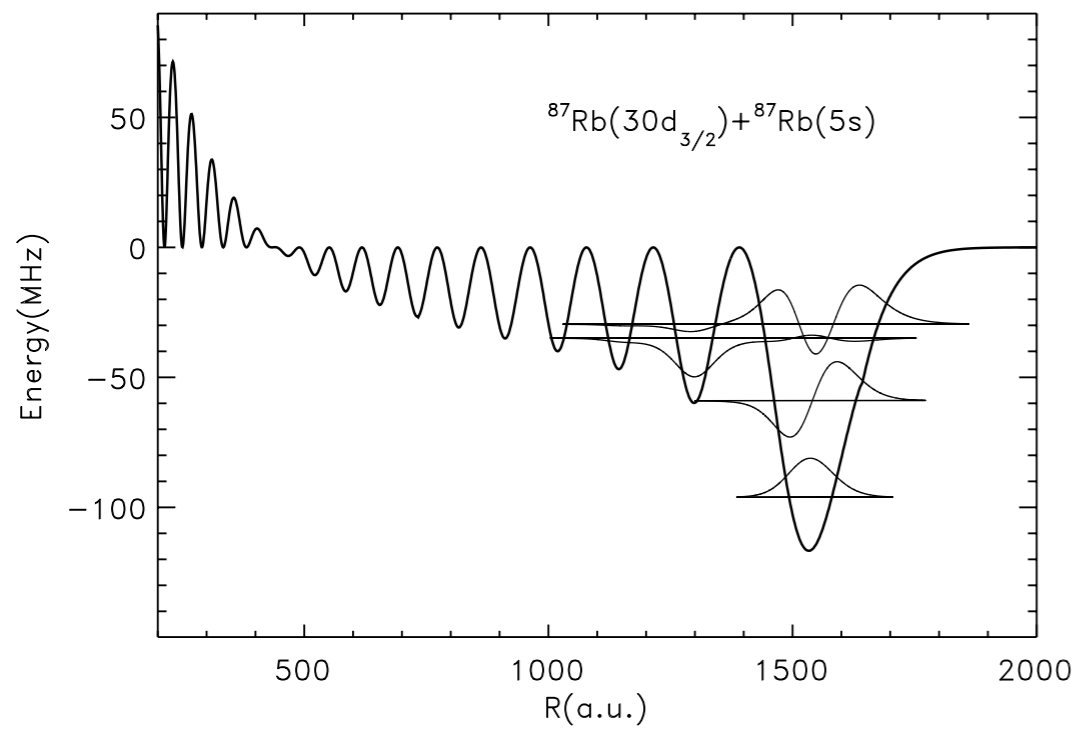
s-wave e⁻ scattering

$^3\Sigma$

p-wave e⁻ scattering

$^3\Sigma$ $^3\Pi$

Rb(30d) + Rb(5s)



Born-Oppenheimer Rydberg molecular potentials

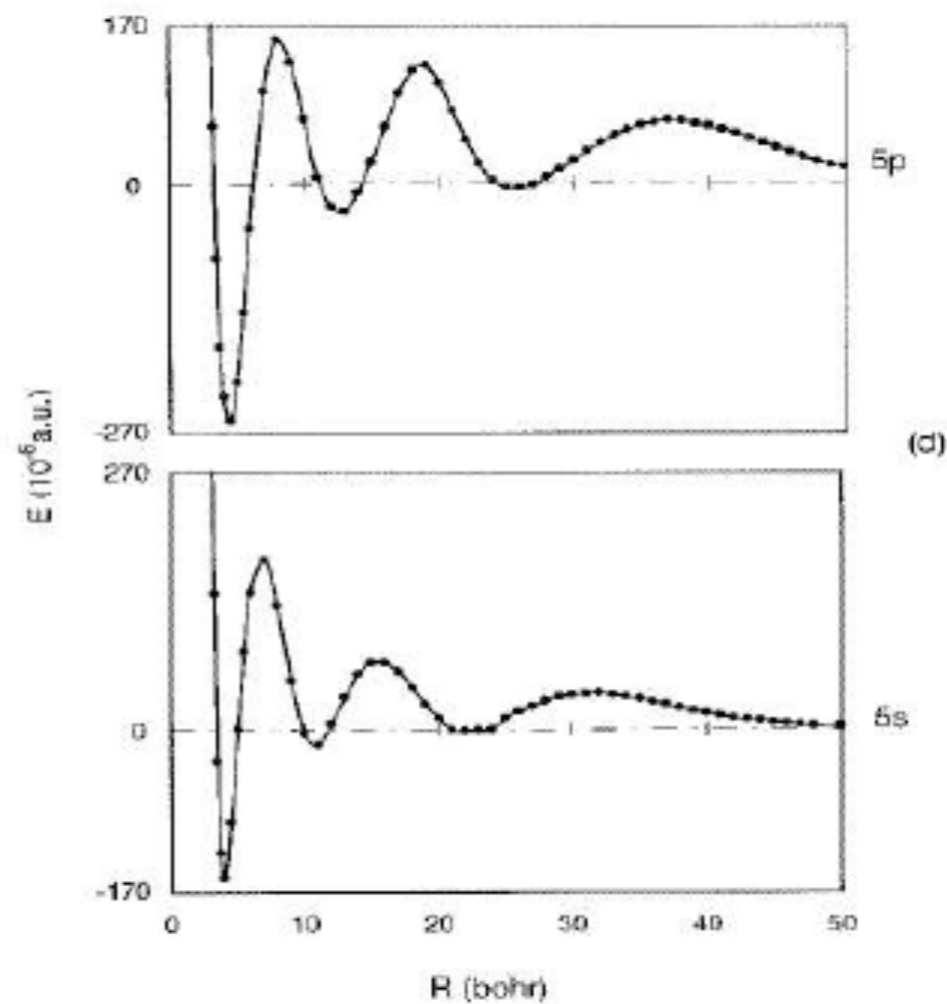
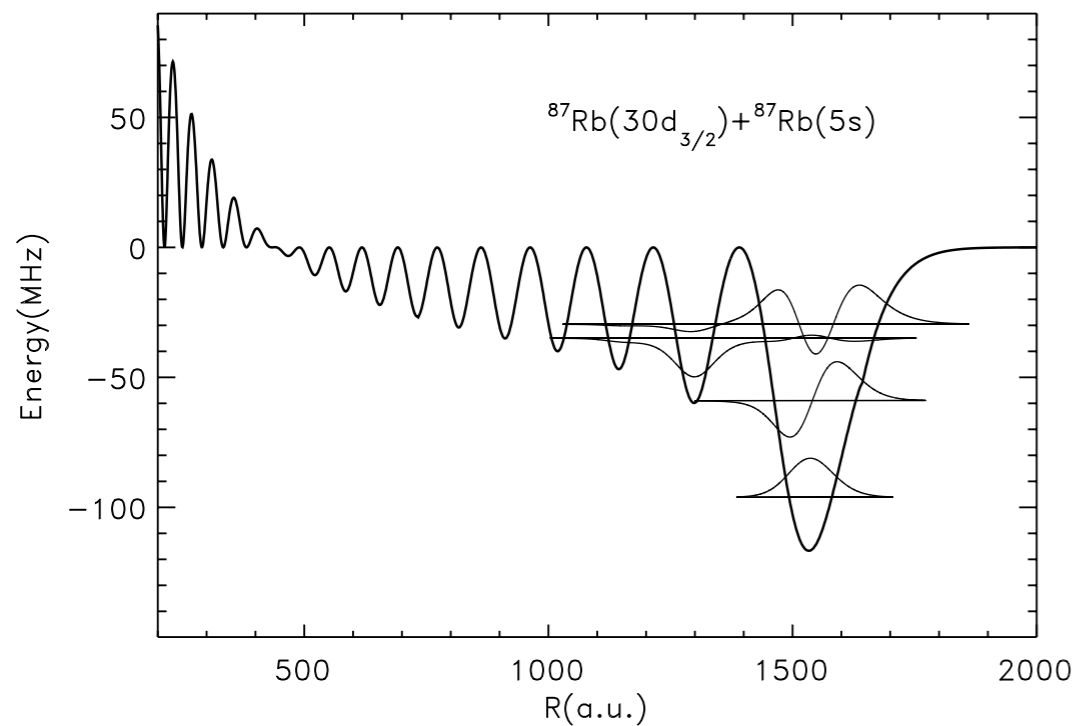
s-wave e⁻ scattering

$^3\Sigma$

p-wave e⁻ scattering

$^3\Sigma$ $^3\Pi$

Rb(30d) + Rb(5s)



LiHe potentials - Jeung PRA 1999
undulations in BO potentials

Born-Oppenheimer Rydberg molecular potentials

s-wave e⁻ scattering

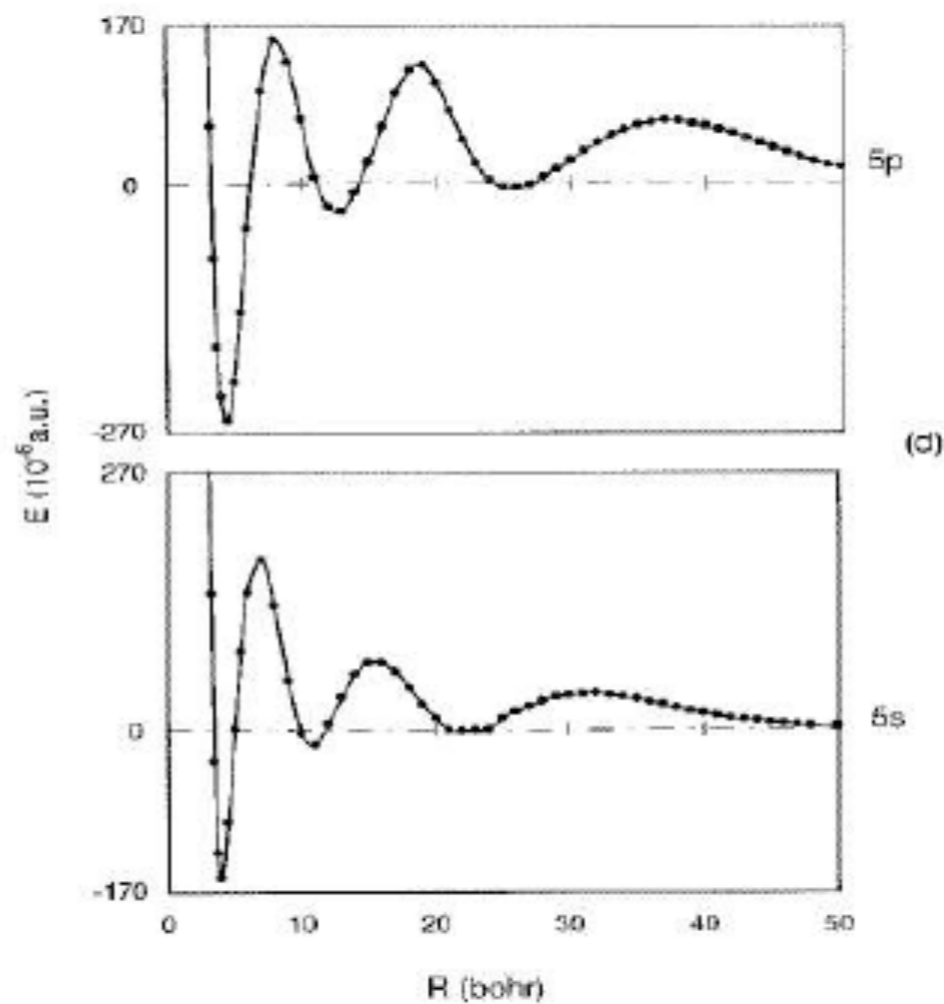
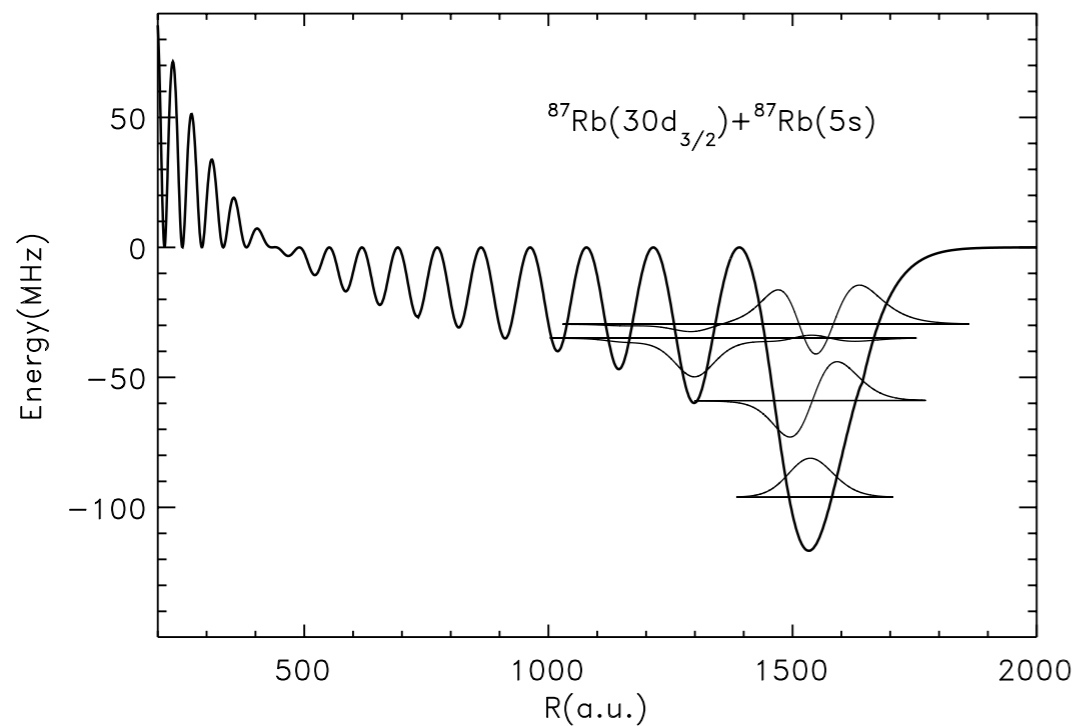
$${}^3\Sigma$$

p-wave e⁻ scattering

$${}^3\Sigma \quad {}^3\Pi$$

$$U_n(R) = -\frac{1}{2n^2} + 2\pi a_T[k(R)]|\psi_{nd0}(\mathbf{R})|^2$$

Rb(30d) + Rb(5s)



LiHe potentials - Jeung PRA 1999
undulations in BO potentials

Experimental Verification of Minima in Excited Long-Range Rydberg States of Rb_2

Chris H. Greene,¹ Edward L. Hamilton,² Heather Crowell,³ Cedomil Vadla,⁴ and Kay Niemax⁵

¹Department of Physics and JILA, University of Colorado, Boulder, Colorado 80309-0440, USA

²Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, USA

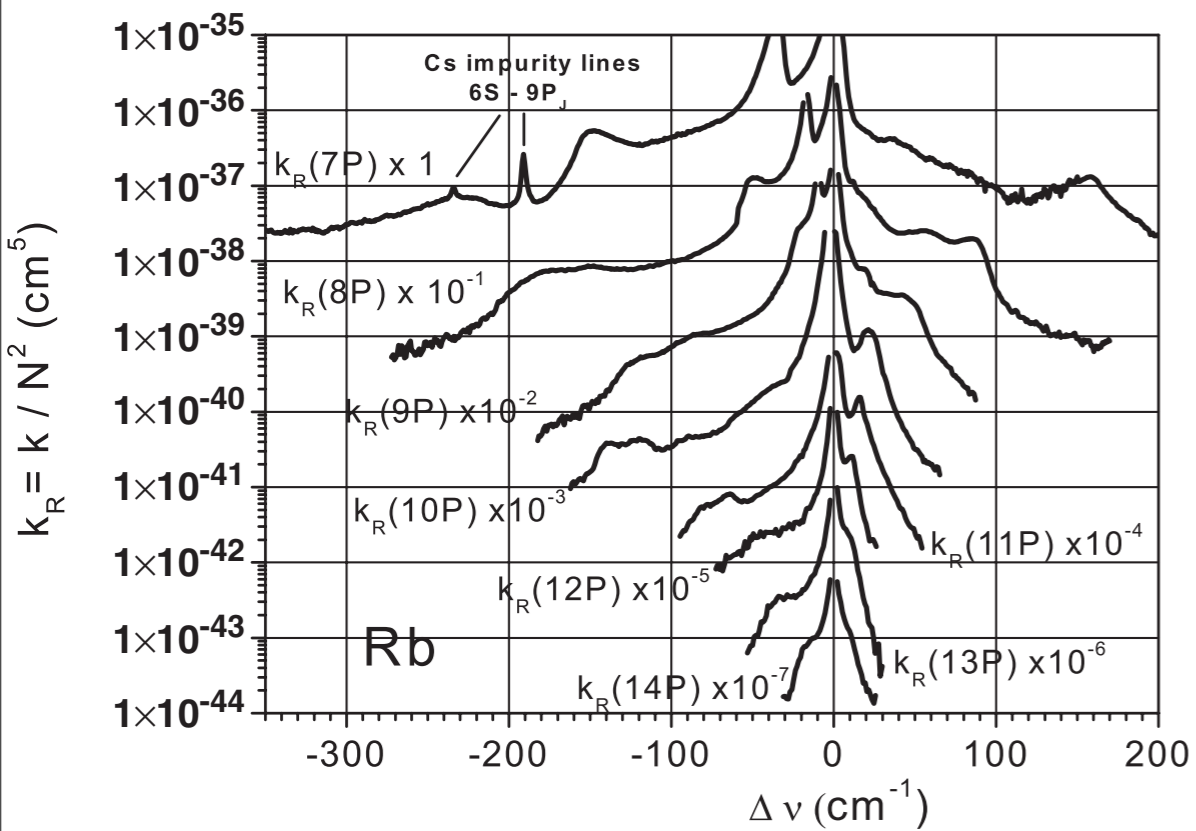
³Department of Chemistry and JILA, University of Colorado, Boulder, Colorado 80309-0440, USA

⁴Institute of Physics, Bijenicka 46, 10000 Zagreb, Croatia

⁵ISAS-Institute for Analytical Sciences at the University of Dortmund, Bunsen-Kirchhoff-Str. 11, D-44139, Dortmund, Germany

(Received 1 September 2006; published 8 December 2006)

Recent theoretical studies with alkali atoms A^* excited to high Rydberg states predicted the existence of ultra-long-range molecular bound states. Such excited dimers have large electric dipole moments which, in combination with their long radiative lifetimes, make them excellent candidates for manipulation in applications. This Letter reports on experimental investigations of the self-broadening of Rb principal series lines, which revealed multiple satellites in the line wings. The positions of the satellites agree quantitatively with theoretically predicted minima in the excited long-range Rydberg states of Rb_2 .



Experimental Verification of Minima in Excited Long-Range Rydberg States of Rb_2

Chris H. Greene,¹ Edward L. Hamilton,² Heather Crowell,³ Cedomil Vadla,⁴ and Kay Niemax⁵

¹Department of Physics and JILA, University of Colorado, Boulder, Colorado 80309-0440, USA

²Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, USA

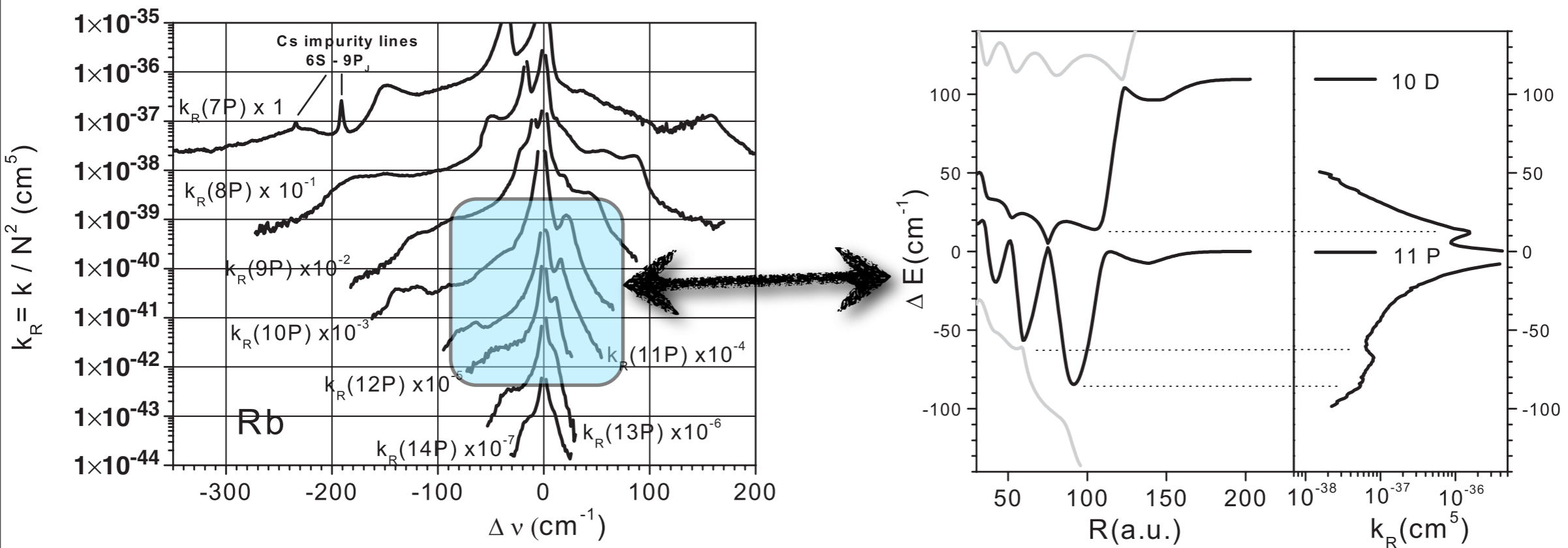
³Department of Chemistry and JILA, University of Colorado, Boulder, Colorado 80309-0440, USA

⁴Institute of Physics, Bijenicka 46, 10000 Zagreb, Croatia

⁵ISAS-Institute for Analytical Sciences at the University of Dortmund, Bunsen-Kirchhoff-Str. 11, D-44139, Dortmund, Germany

(Received 1 September 2006; published 8 December 2006)

Recent theoretical studies with alkali atoms A^* excited to high Rydberg states predicted the existence of ultra-long-range molecular bound states. Such excited dimers have large electric dipole moments which, in combination with their long radiative lifetimes, make them excellent candidates for manipulation in applications. This Letter reports on experimental investigations of the self-broadening of Rb principal series lines, which revealed multiple satellites in the line wings. The positions of the satellites agree quantitatively with theoretically predicted minima in the excited long-range Rydberg states of Rb_2 .



Beyond s-wave ...

$$\langle k_f | V(\mathbf{r} - \mathbf{R}) | k_i \rangle = -\frac{2\pi}{k} \sum_l (2l + 1) \tan(\delta_l) P_l(k_i \cdot k_f)$$

$$\langle j | V(\mathbf{r} - \mathbf{R}) | i \rangle = -\frac{2\pi}{k} \sum_l (2l + 1) \tan(\delta_l) \Psi_j^*(\mathbf{R}) \Psi_i(\mathbf{R}) P_l(\nabla' \cdot \nabla / k^2)$$

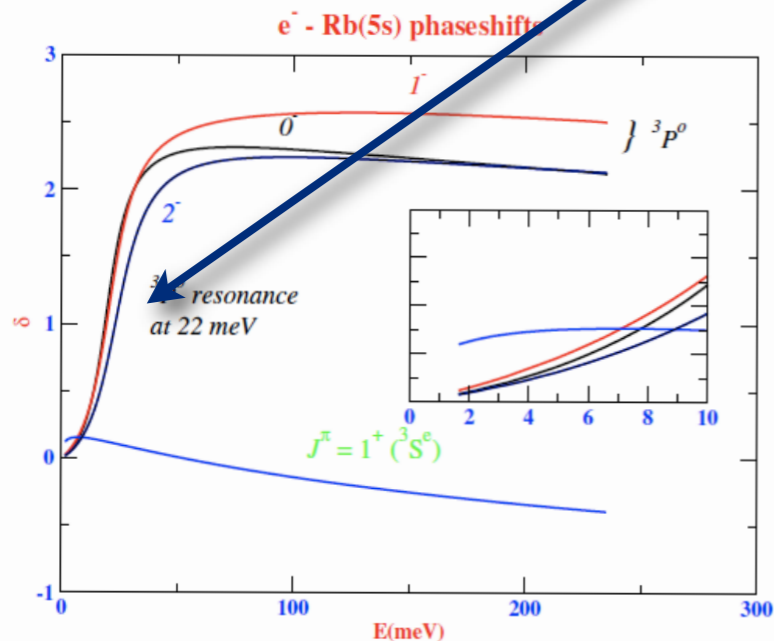
Beyond s-wave ...

$$\langle k_f | V(\mathbf{r} - \mathbf{R}) | k_i \rangle = -\frac{2\pi}{k} \sum_l (2l + 1) \tan(\delta_l) P_l(k_i \cdot k_f)$$

$$\langle j | V(\mathbf{r} - \mathbf{R}) | i \rangle = -\frac{2\pi}{k} \sum_l (2l + 1) \tan(\delta_l) \Psi_j^*(\mathbf{R}) \Psi_i(\mathbf{R}) P_l(\nabla' \cdot \nabla / k^2)$$

$$V_s(\vec{r}, \vec{R}) = 2\pi A_T [k(R)] \delta(\vec{r} - \vec{R}) \quad A_T = -\tan \delta_0^T / k$$

$$\langle \Psi_1 | V_p | \Psi_2 \rangle = -\frac{6\pi \tan \delta_1^T}{k^3(R)} \vec{\nabla} \Psi_1(\vec{R}) \cdot \vec{\nabla}' \Psi_2(\vec{R})$$



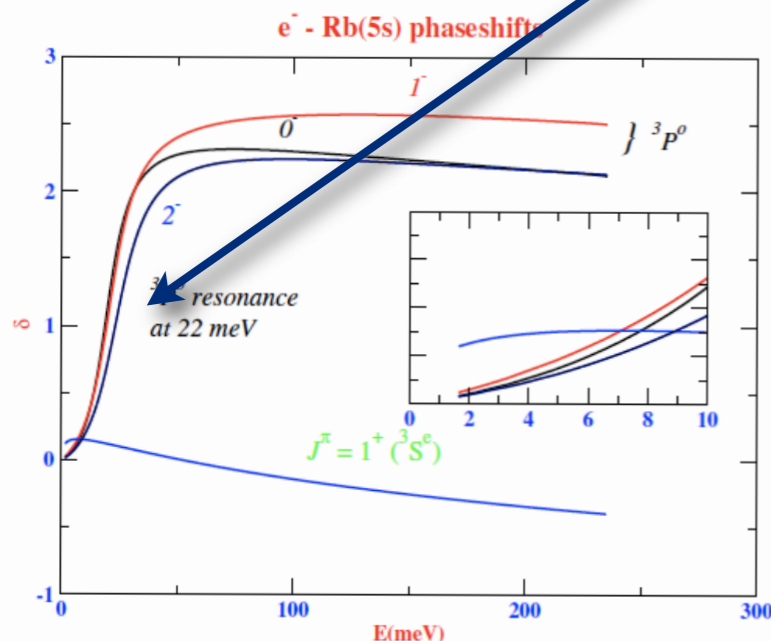
Beyond s-wave ...

$$\langle k_f | V(\mathbf{r} - \mathbf{R}) | k_i \rangle = -\frac{2\pi}{k} \sum_l (2l + 1) \tan(\delta_l) P_l(k_i \cdot k_f)$$

$$\langle j | V(\mathbf{r} - \mathbf{R}) | i \rangle = -\frac{2\pi}{k} \sum_l (2l + 1) \tan(\delta_l) \Psi_j^*(\mathbf{R}) \Psi_i(\mathbf{R}) P_l(\nabla' \cdot \nabla / k^2)$$

$$V_s(\vec{r}, \vec{R}) = 2\pi A_T [k(R)] \delta(\vec{r} - \vec{R}) \quad A_T = -\tan \delta_0^T / k$$

$$\langle \Psi_1 | V_p | \Psi_2 \rangle = -\frac{6\pi \tan \delta_1^T}{k^3(R)} \vec{\nabla} \Psi_1(\vec{R}) \cdot \vec{\nabla}' \Psi_2(\vec{R})$$



... creates two molecular classes: one which maximizes gradient perp to R, and one which maximizes gradient para to R

Weibin ... numerical tour-de-force

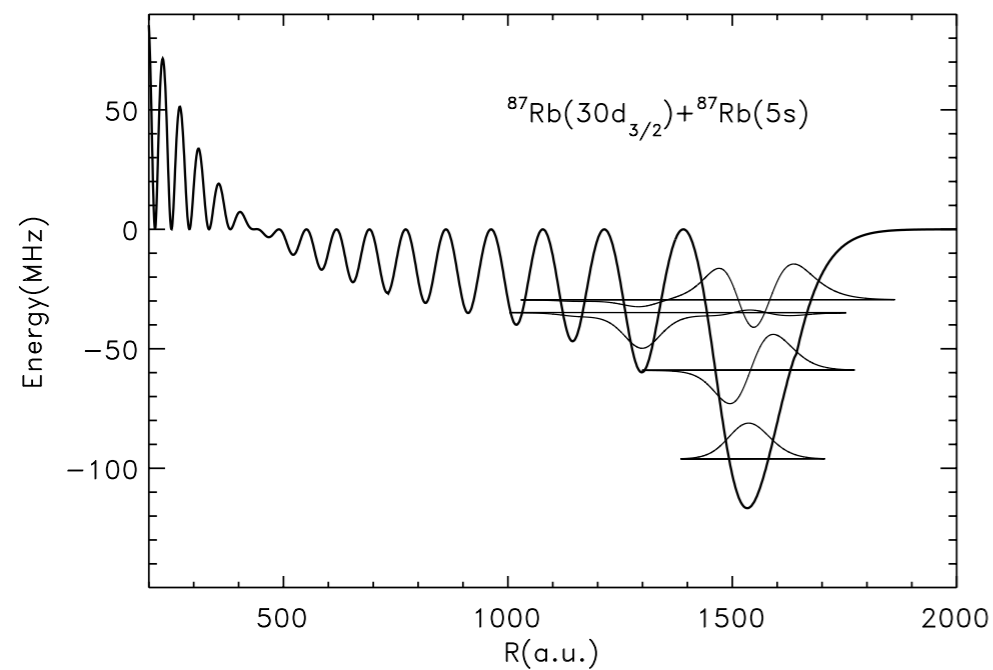
Exotic molecules?

Rb(5s)+Rb(ns) ; $\mu_s = 3.13$

Rb(5s)+Rb(np_{1/2,3/2}); $\mu_p = 1.67$

Rb(5s)+Rb(nd_{3/2,5/2}); $\mu_d = 1.35$

$$U_n(R) = -\frac{1}{2n^2} + 2\pi a_T[k(R)]|\psi_{nd0}(\mathbf{R})|^2$$



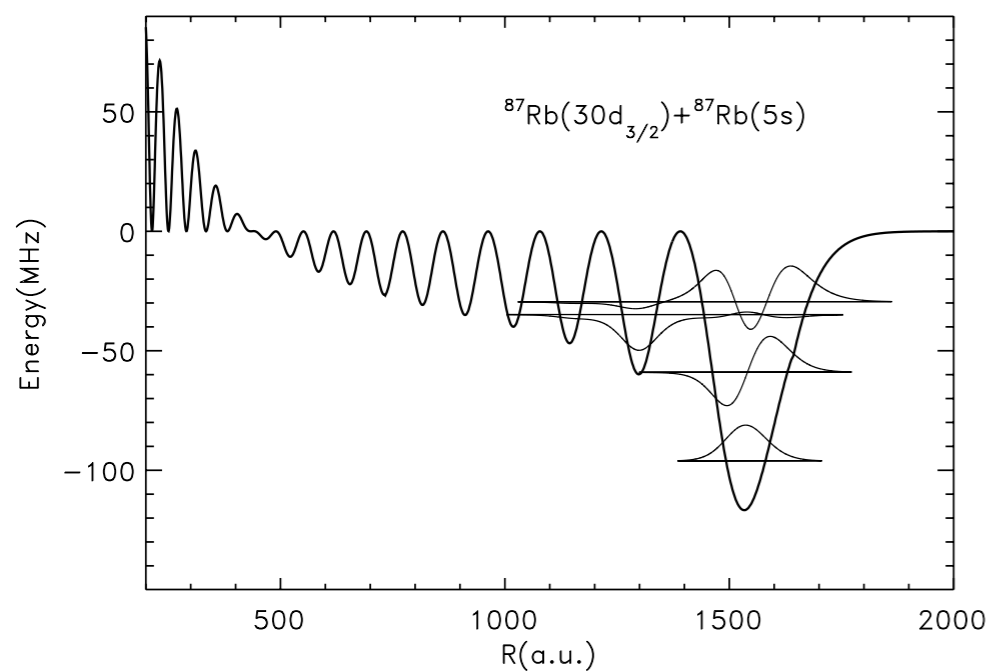
Exotic molecules?

Rb(5s)+Rb(ns) ; $\mu_s = 3.13$

Rb(5s)+Rb(np_{1/2,3/2}); $\mu_p = 1.67$

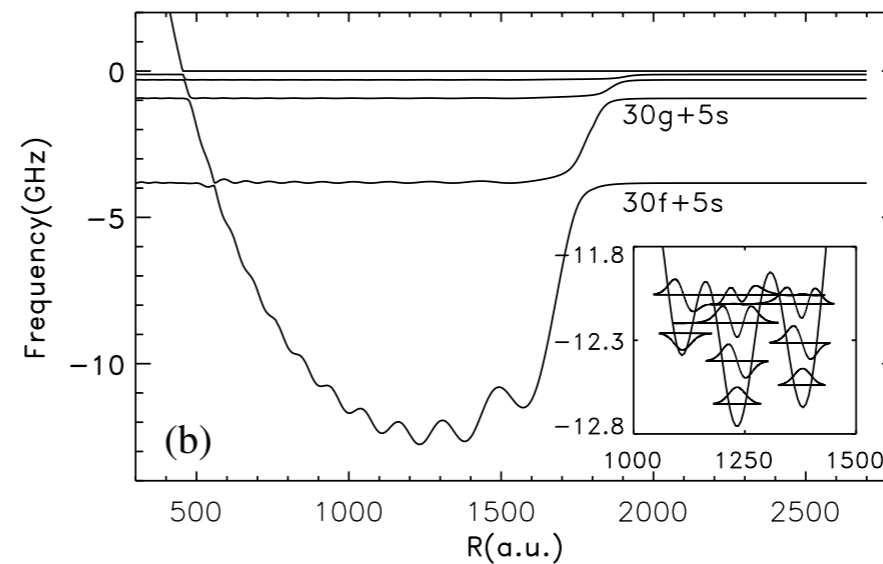
Rb(5s)+Rb(nd_{3/2,5/2}); $\mu_d = 1.35$

$$U_n(R) = -\frac{1}{2n^2} + 2\pi a_T[k(R)]|\psi_{nd0}(\mathbf{R})|^2$$



Rb(5s)+Rb(nl>2); $\mu_d \sim 0$

$$U_n(R) = -\frac{1}{2n^2} + 2\pi a_T[k(R)] \sum_{l=l_{\min}}^{n-1} \frac{2l+1}{4\pi} |R_{nl}(R)|^2$$



Exotic molecules?

Rb(5s)+Rb(ns) ; $\mu_s = 3.13$

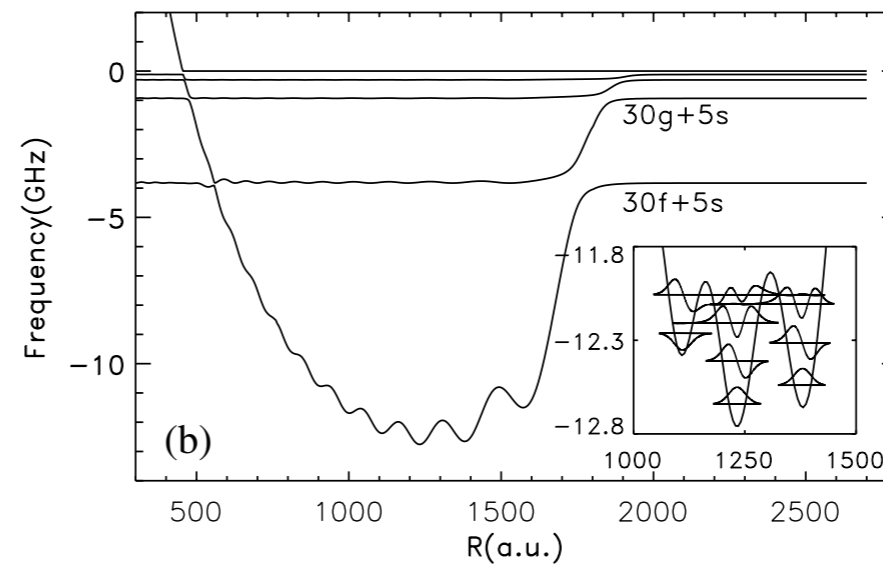
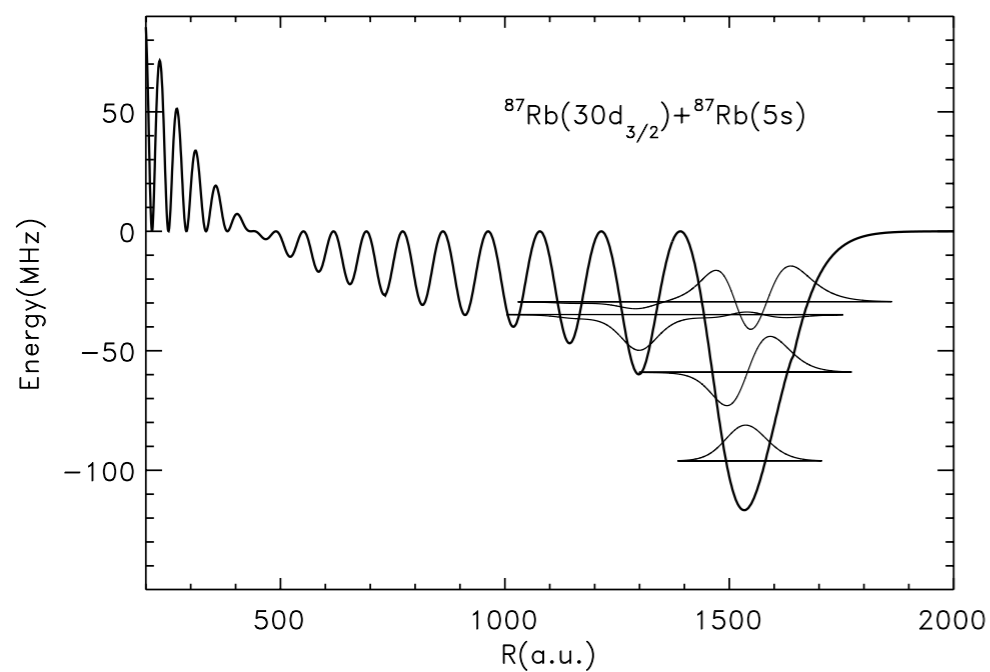
Rb(5s)+Rb(np_{1/2,3/2}); $\mu_p = 1.67$

Rb(5s)+Rb(nd_{3/2,5/2}); $\mu_d = 1.35$

Rb(5s)+Rb(nl>2); $\mu_d \sim 0$

$$U_n(R) = -\frac{1}{2n^2} + 2\pi a_T[k(R)] \sum_{l=l_{\min}}^{n-1} \frac{2l+1}{4\pi} |R_{nl}(R)|^2$$

$$U_n(R) = -\frac{1}{2n^2} + 2\pi a_T[k(R)] |\psi_{nd0}(\mathbf{R})|^2$$



s-wave

Exotic molecules?

Rb(5s)+Rb(ns) ; $\mu_s = 3.13$

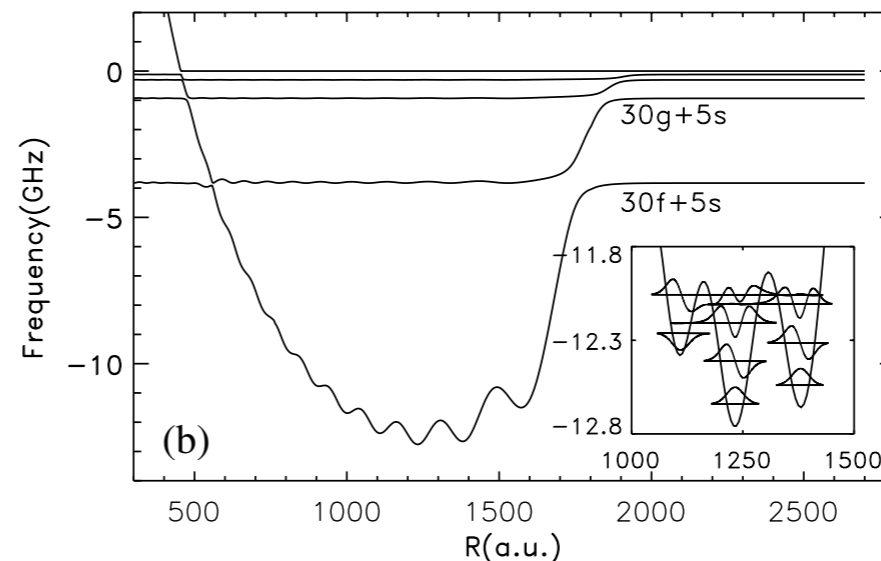
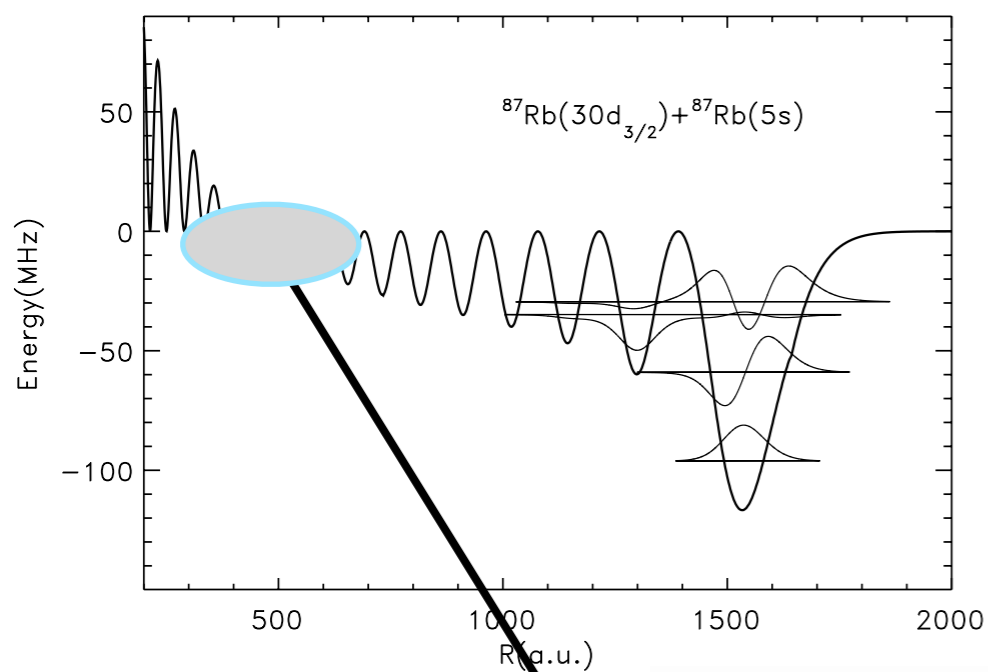
Rb(5s)+Rb(np_{1/2,3/2}) ; $\mu_p = 1.67$

Rb(5s)+Rb(nd_{3/2,5/2}) ; $\mu_d = 1.35$

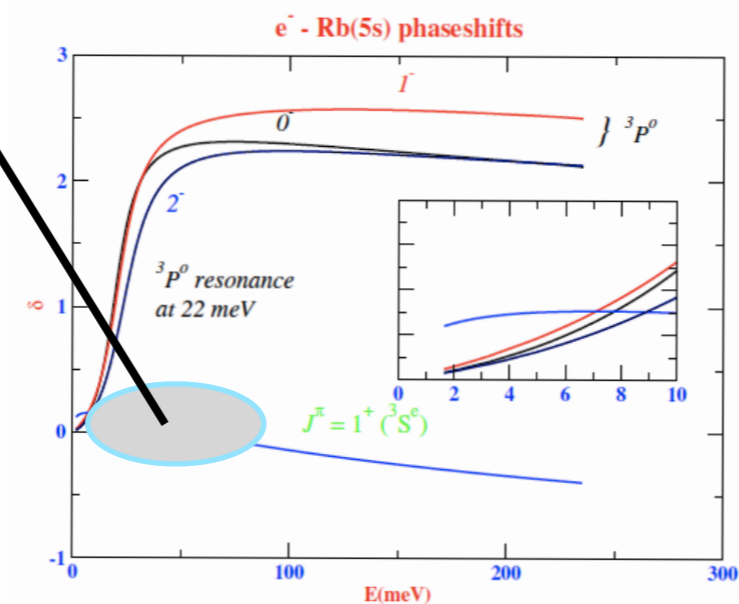
Rb(5s)+Rb(nl>2); $\mu_d \sim 0$

$$U_n(R) = -\frac{1}{2n^2} + 2\pi a_T[k(R)] \sum_{l=l_{min}}^{n-1} \frac{2l+1}{4\pi} |R_{nl}(R)|^2$$

$$U_n(R) = -\frac{1}{2n^2} + 2\pi a_T[k(R)] |\psi_{nd0}(\mathbf{R})|^2$$



s-wave



Exotic molecules?

Rb(5s)+Rb(ns) ; $\mu_s = 3.13$

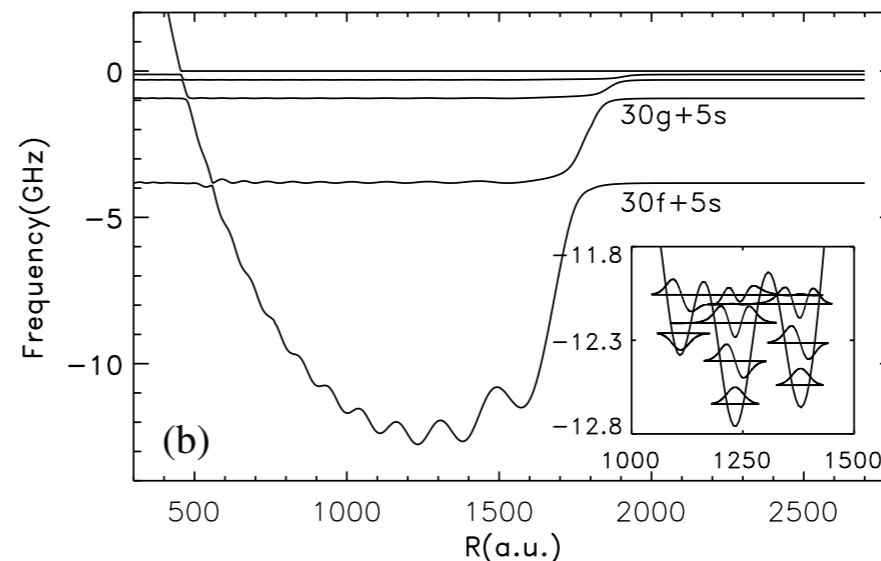
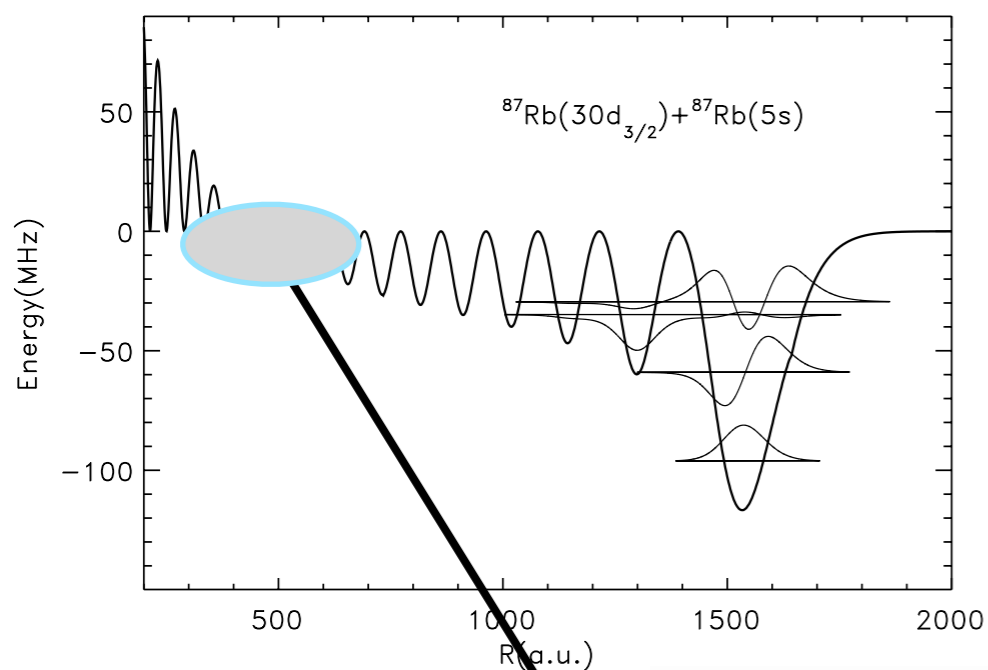
Rb(5s)+Rb(np_{1/2,3/2}) ; $\mu_p = 1.67$

Rb(5s)+Rb(nd_{3/2,5/2}) ; $\mu_d = 1.35$

Rb(5s)+Rb(nl>2); $\mu_d \sim 0$

$$U_n(R) = -\frac{1}{2n^2} + 2\pi a_T[k(R)] \sum_{l=l_{min}}^{n-1} \frac{2l+1}{4\pi} |R_{nl}(R)|^2$$

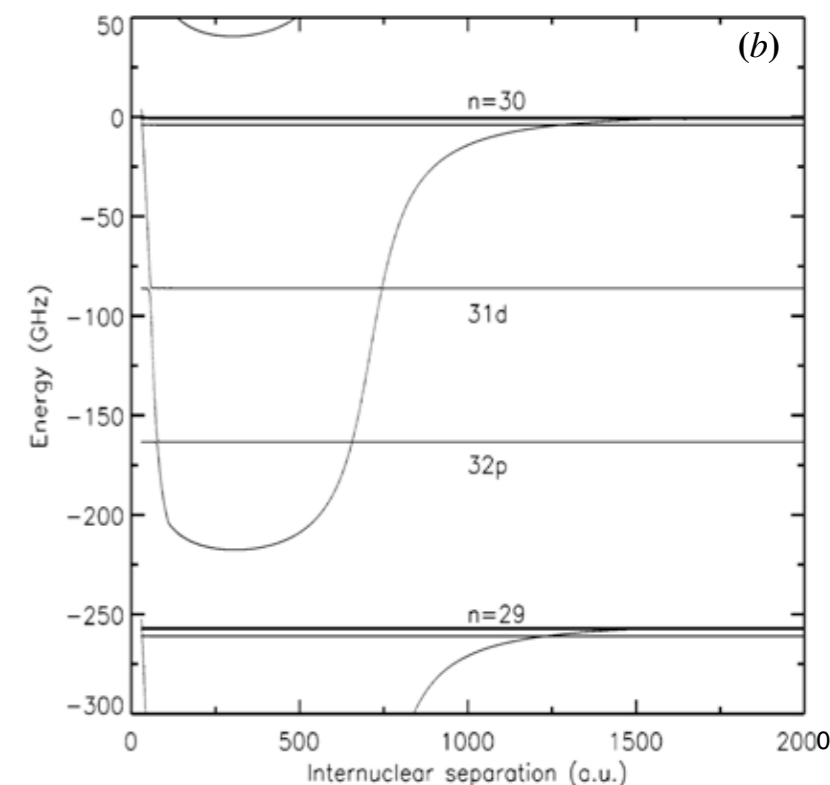
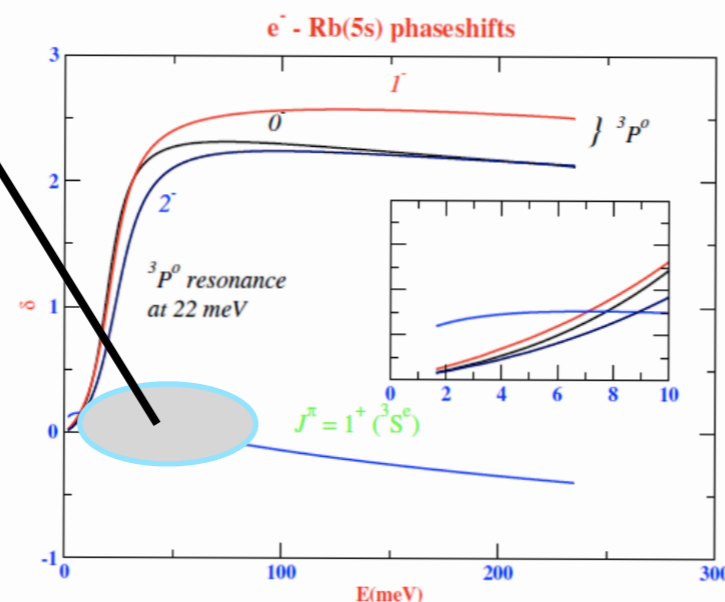
$$U_n(R) = -\frac{1}{2n^2} + 2\pi a_T[k(R)] |\psi_{nd0}(\mathbf{R})|^2$$



s-wave

$$\langle \Psi_1 | V_p | \Psi_2 \rangle = -\frac{6\pi \tan \delta_1^T}{k^3(R)} \vec{\nabla} \Psi_1(\vec{R}) \cdot \vec{\nabla}' \Psi_2(\vec{R})$$

p-wave



Exotic molecules?

Rb(5s)+Rb(ns) ; $\mu_s = 3.13$

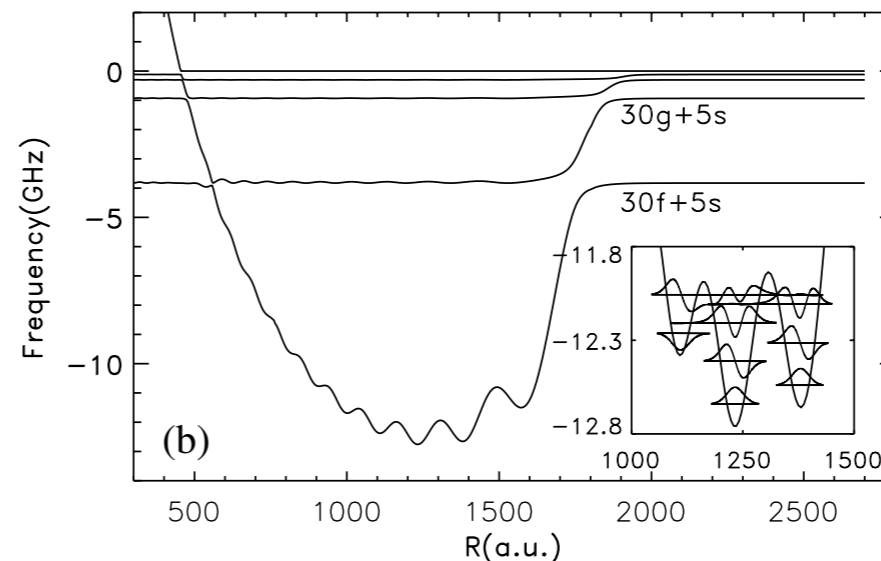
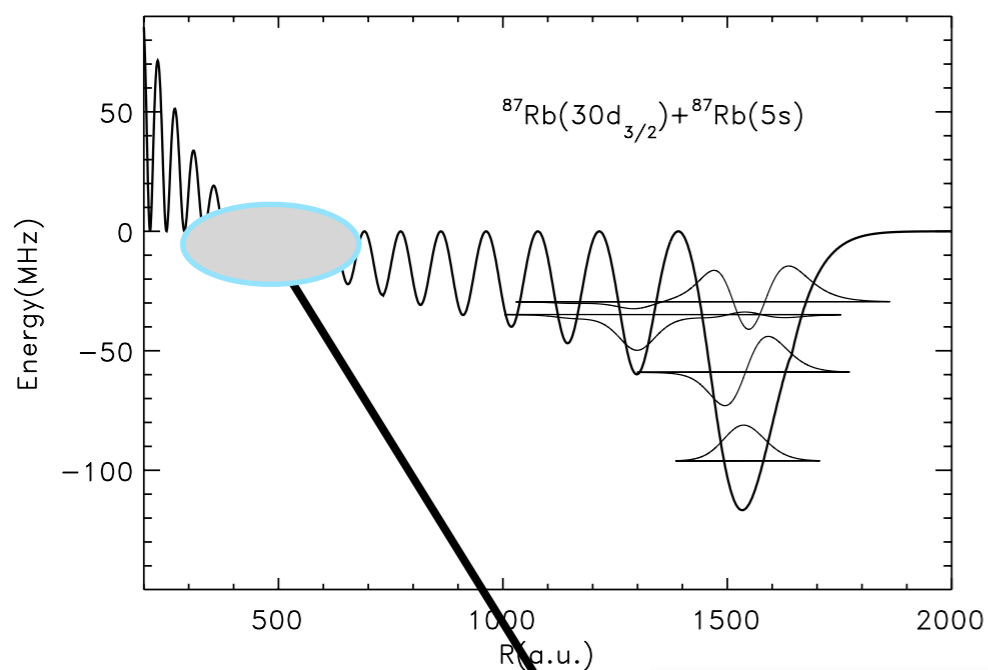
Rb(5s)+Rb(np_{1/2,3/2}) ; $\mu_p = 1.67$

Rb(5s)+Rb(nd_{3/2,5/2}) ; $\mu_d = 1.35$

Rb(5s)+Rb(nl>2); $\mu_d \sim 0$

$$U_n(R) = -\frac{1}{2n^2} + 2\pi a_T[k(R)] \sum_{l=l_{min}}^{n-1} \frac{2l+1}{4\pi} |R_{nl}(R)|^2$$

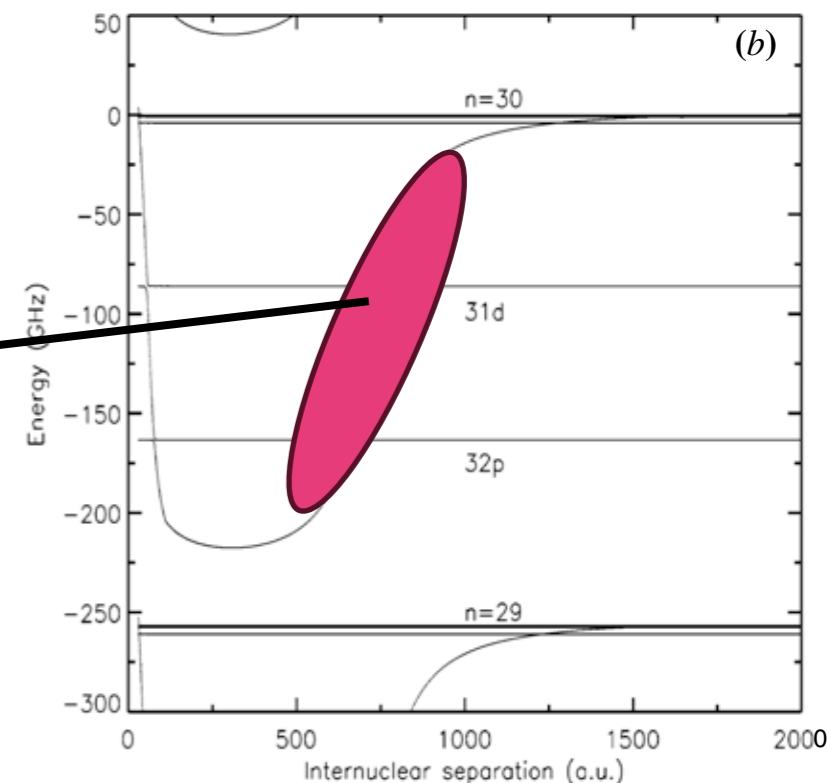
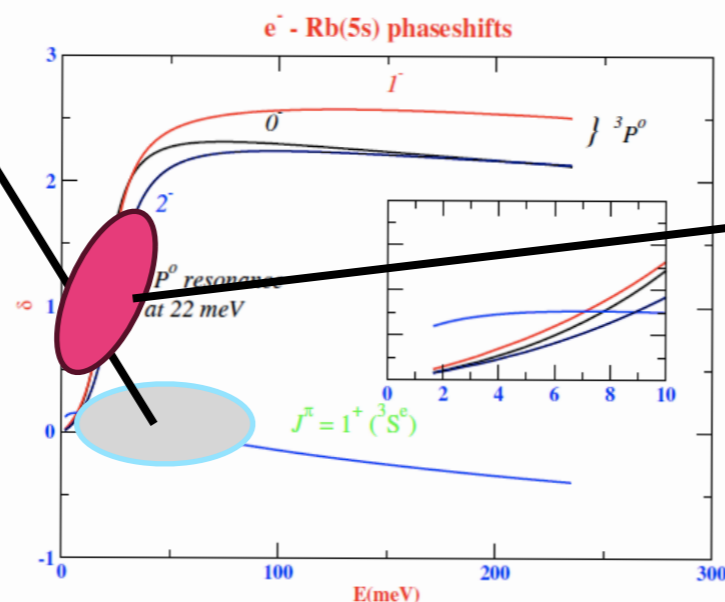
$$U_n(R) = -\frac{1}{2n^2} + 2\pi a_T[k(R)] |\psi_{nd0}(\mathbf{R})|^2$$



s-wave

$$\langle \Psi_1 | V_p | \Psi_2 \rangle = -\frac{6\pi \tan \delta_1^T}{k^3(R)} \vec{\nabla} \Psi_1(\vec{R}) \cdot \vec{\nabla}' \Psi_2(\vec{R})$$

p-wave



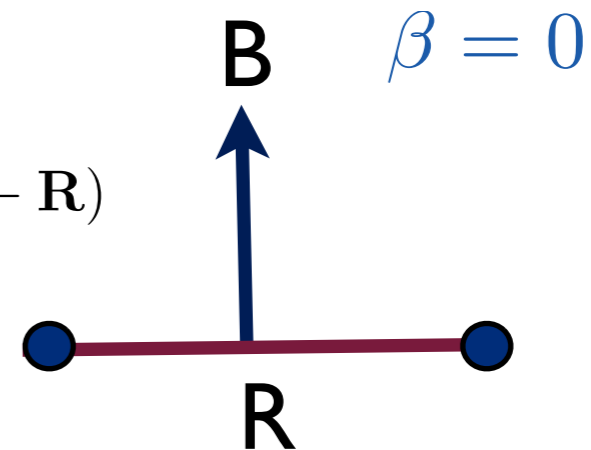
$$H = \frac{1}{2}\mathbf{p}^2 + V(\mathbf{r}) + \frac{1}{2}\mathbf{B} \cdot \mathbf{L} + \frac{1}{8} [\mathbf{B} \times \mathbf{r}]^2 + 2\pi A_T[k(R)]\delta(\mathbf{r} - \mathbf{R})$$

Lesanovsky et al. (2005)

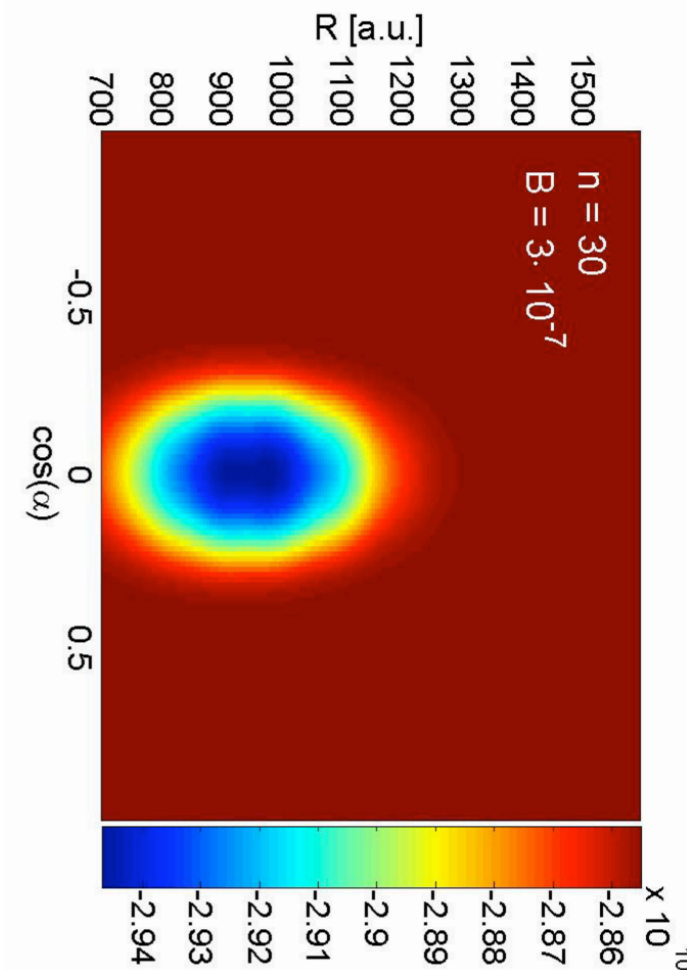
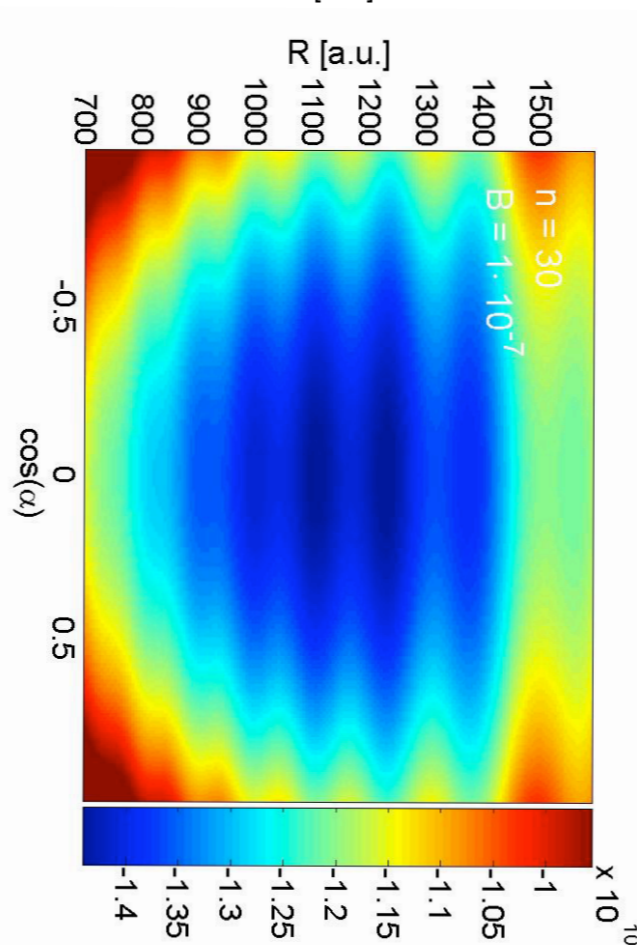
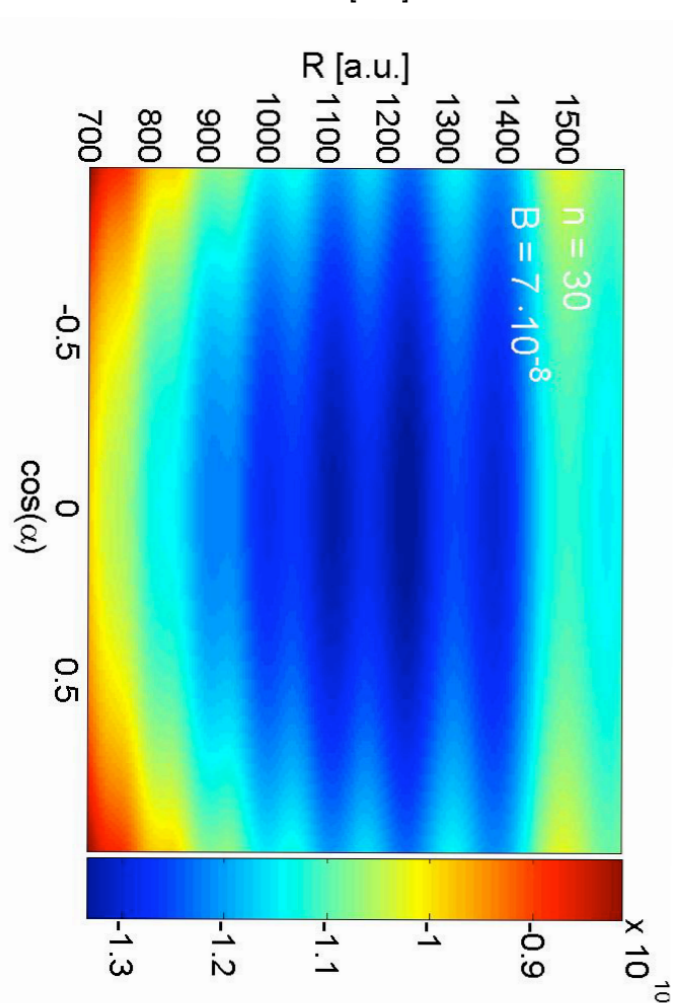
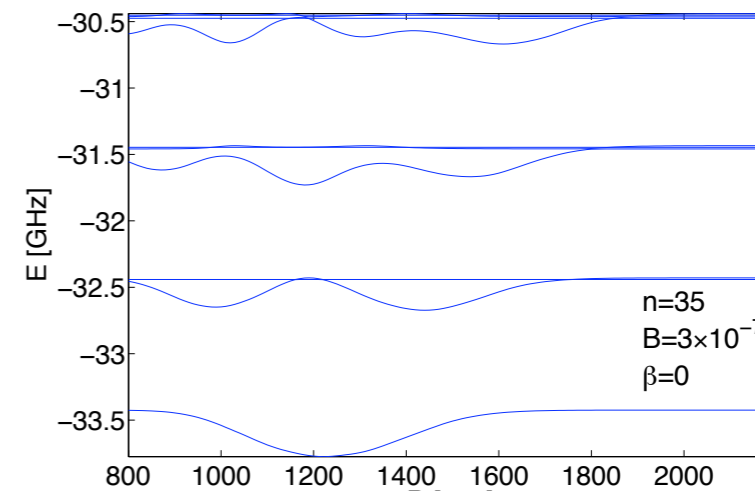
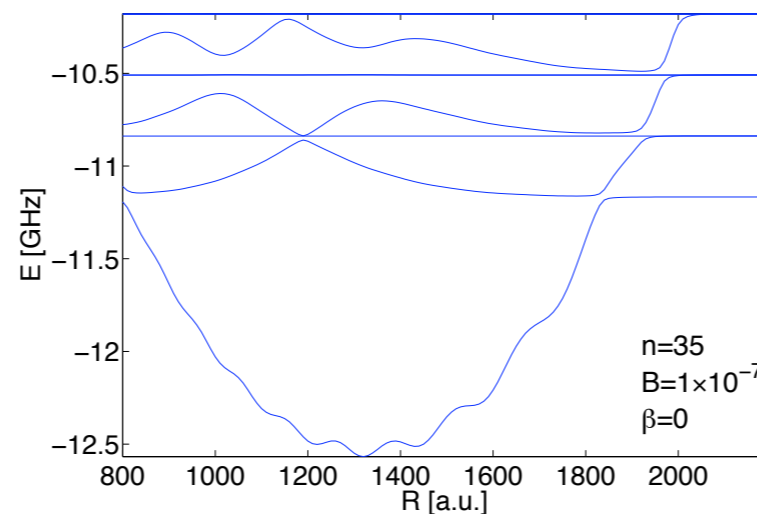
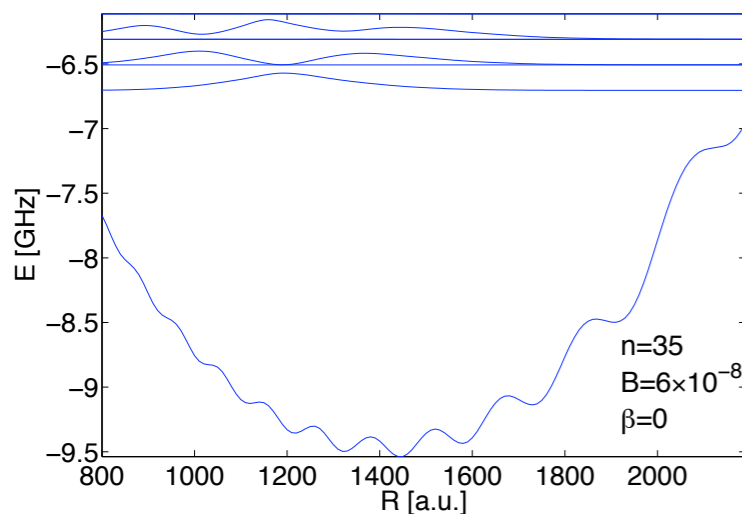
Magnetized trilobites

$$H = \frac{1}{2}\mathbf{p}^2 + V(\mathbf{r}) + \frac{1}{2}\mathbf{B} \cdot \mathbf{L} + \frac{1}{8}[\mathbf{B} \times \mathbf{r}]^2 + 2\pi A_T[k(R)]\delta(\mathbf{r} - \mathbf{R})$$

$$\beta = \frac{\pi}{2} - \cos^{-1}[\hat{B} \cdot \hat{R}]$$



Lesanovsky et al. (2005)

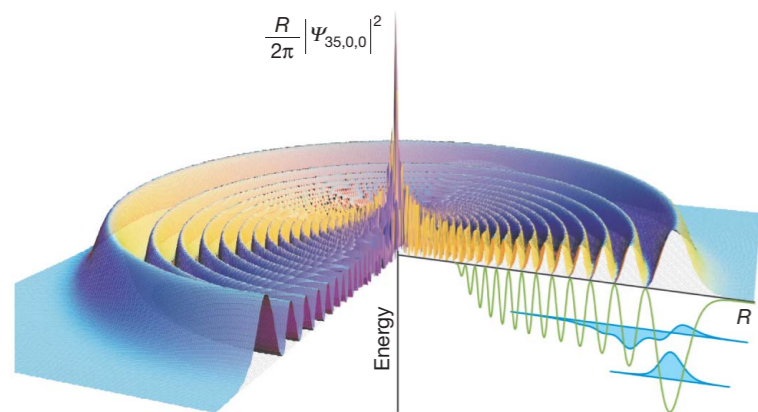
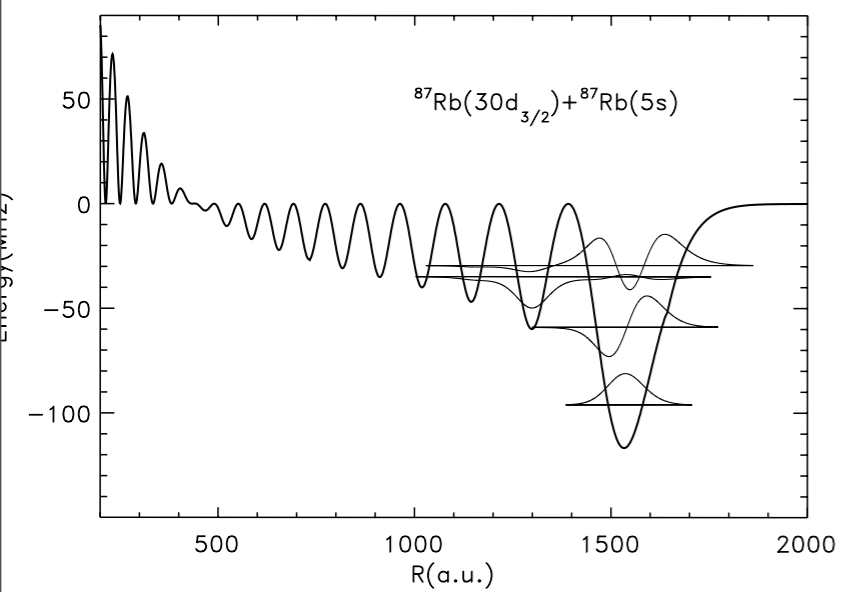


Three cases:

Three cases:

a case of

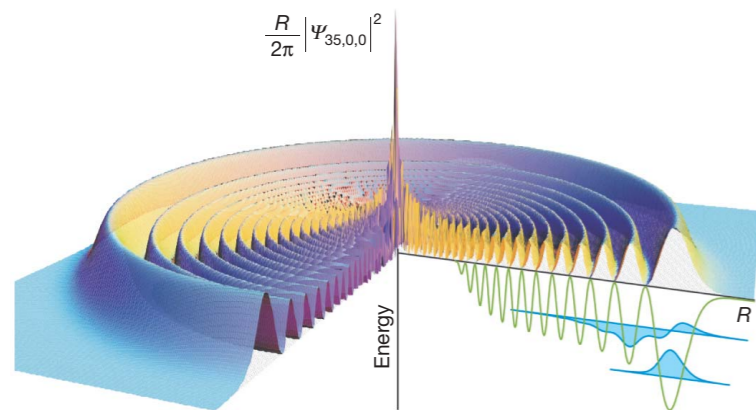
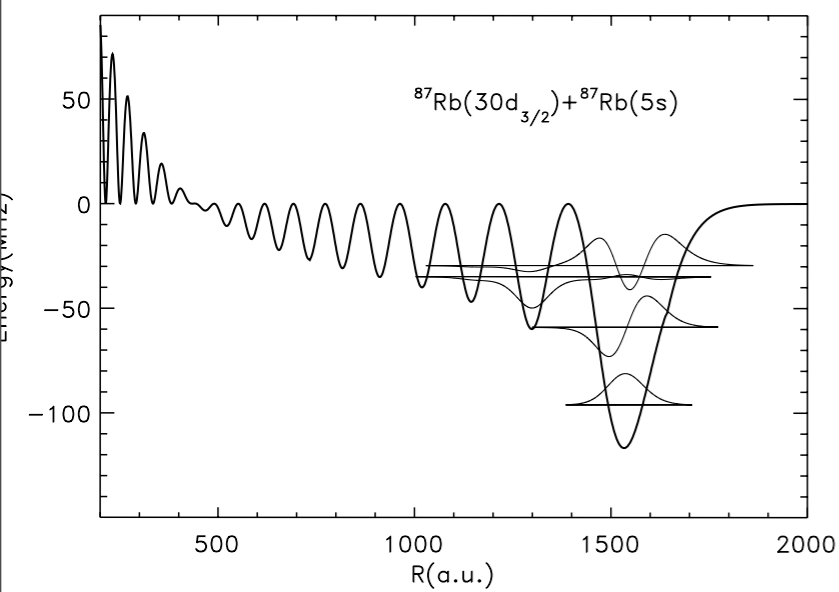
no dipole... well!



Three cases:

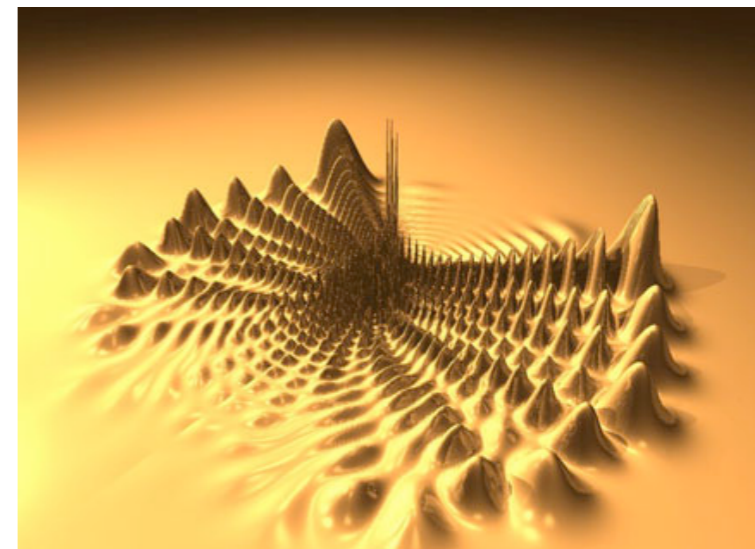
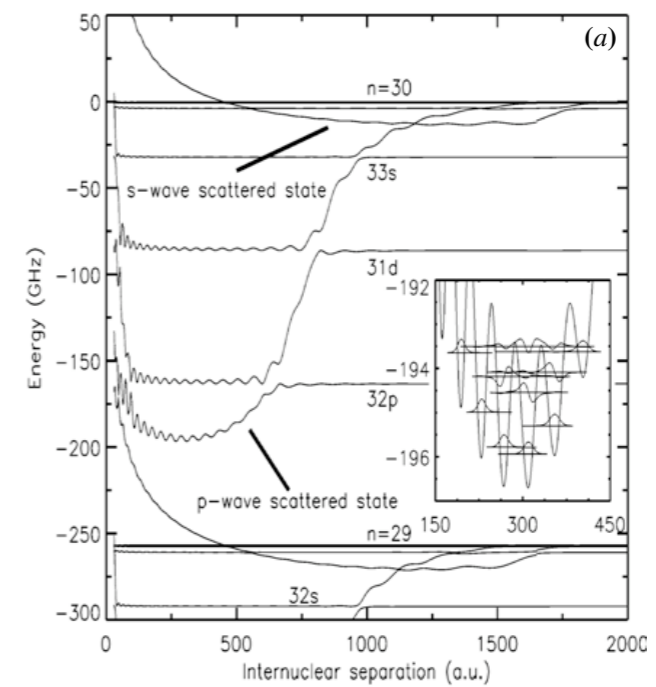
a case of

no dipole... well!



... a case of
butterflies!

large dipole



Three cases:

a case of

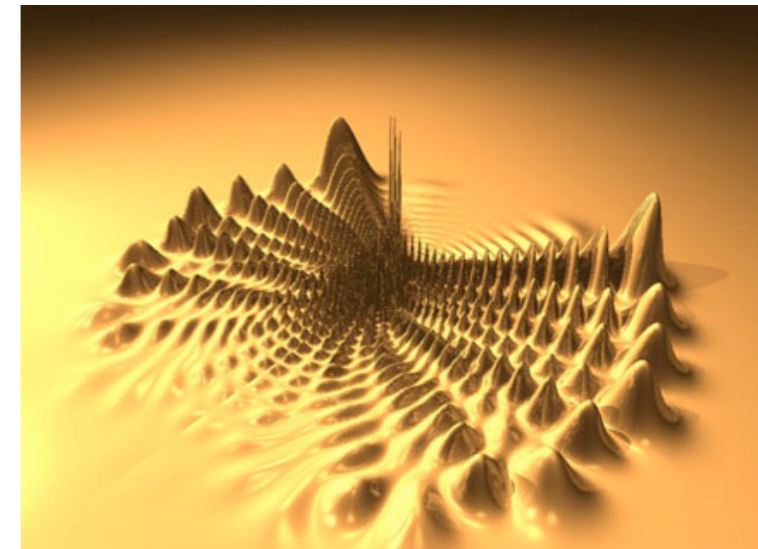
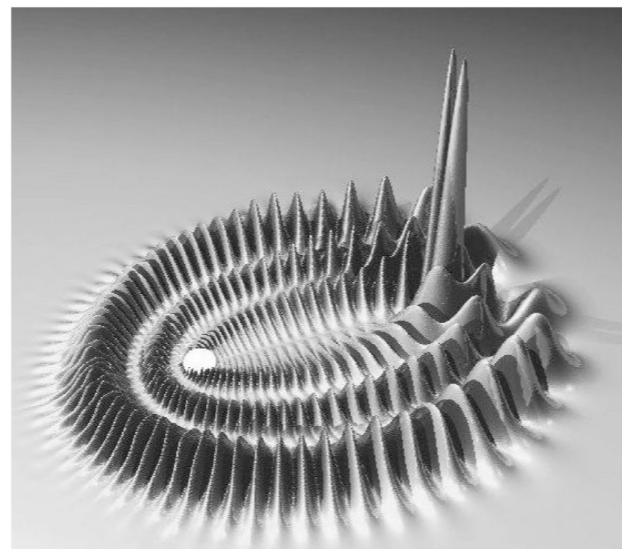
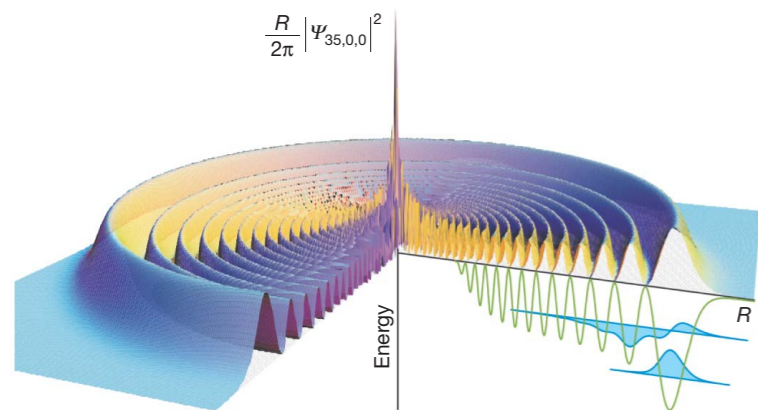
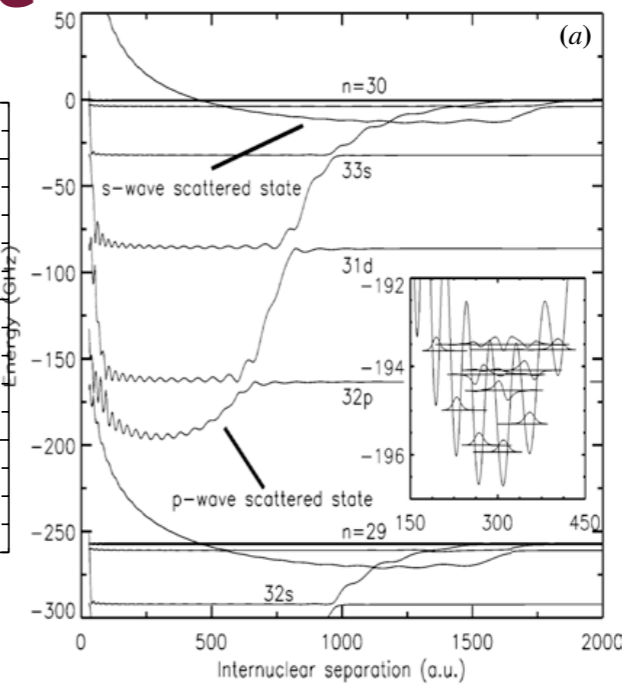
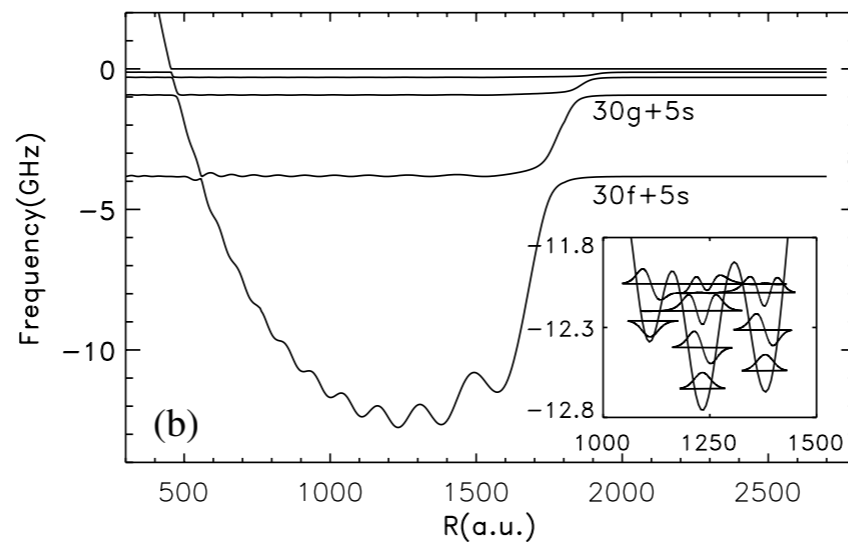
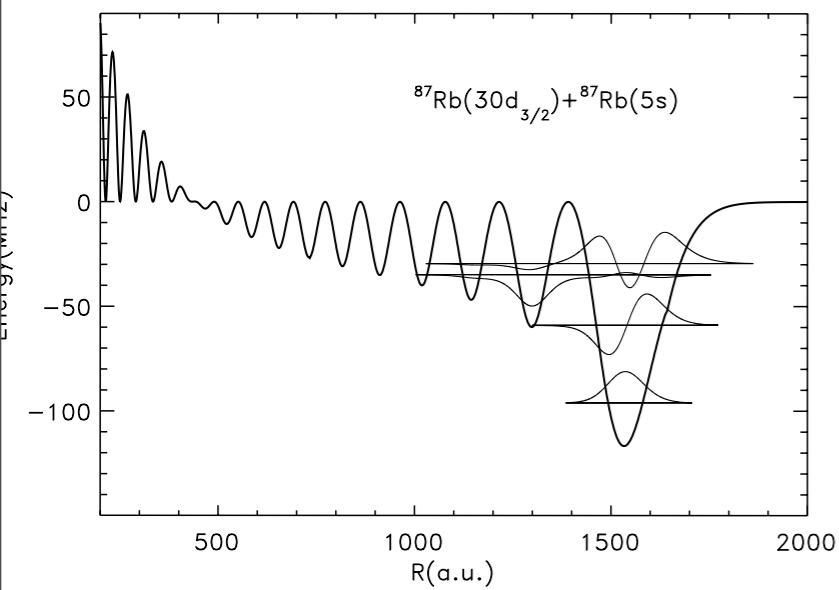
no dipole... well!

... and a case of trilobites!

and even larger dipole

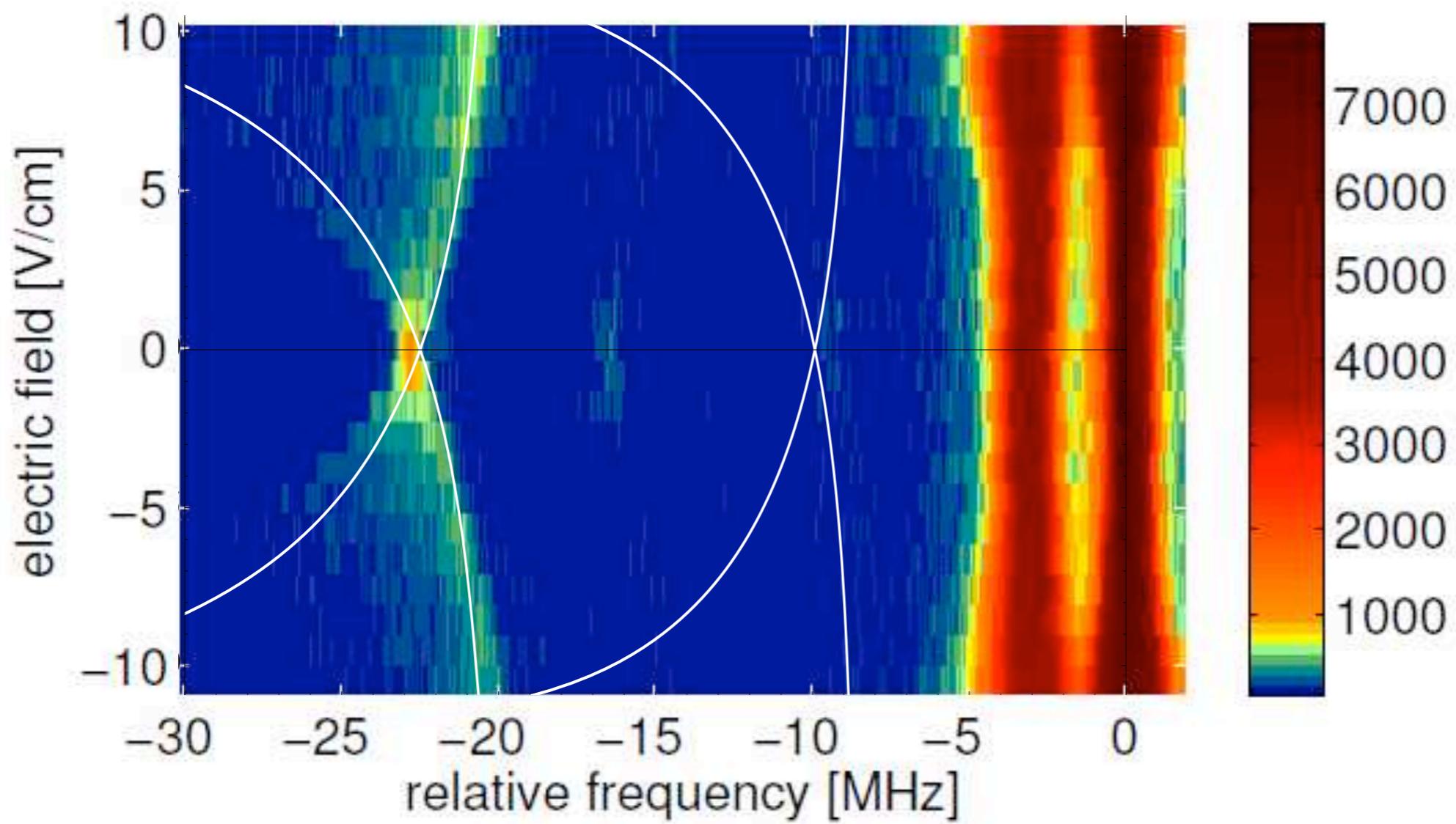
... a case of butterflies!

large dipole

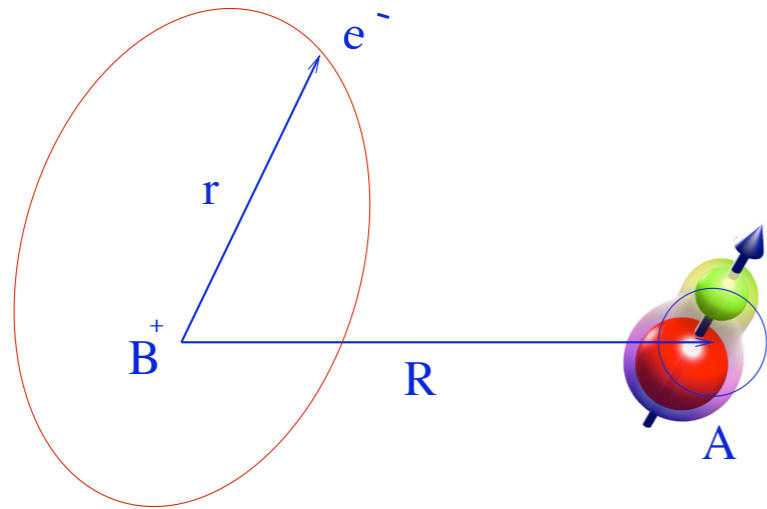


Stark-spectrum

subtracting atomic Stark-shift



Switching gear ...



... no longer short range
scattering length picture does not hold

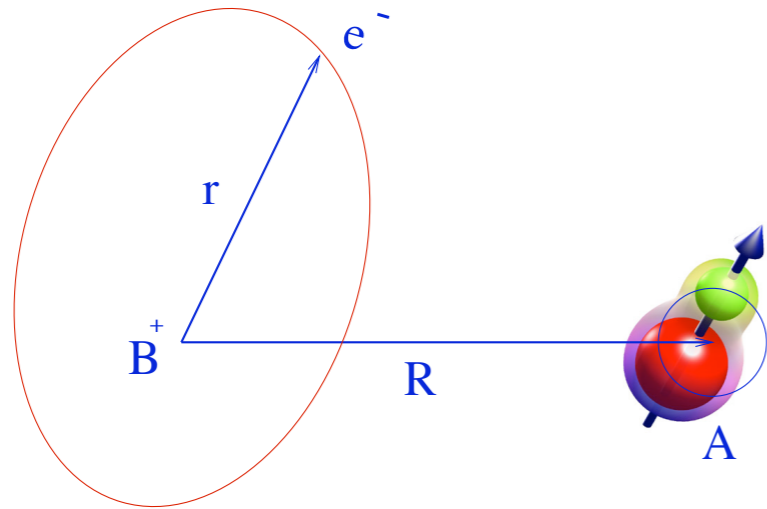
e^- - dipole interaction:

$$\lambda(\lambda + 1)/R^2 = (a - 1/4)/R^2$$

$a > a_c = 0.639$ a.u. = 1.63 D ... Fermi-Teller dipole

... e^- - binds to dipole (supercritical dipole) ... negative ion forms

Switching gear ...



Seth Rittenhouse... (last week)

... no longer short range scattering length picture does not hold

e^- - dipole interaction:

$$\lambda(\lambda + 1)/R^2 = (a - 1/4)/R^2$$

$a > a_c = 0.639 \text{ a.u.} = 1.63 \text{ D} \dots$ Fermi-Teller dipole

... e^- - binds to dipole (supercritical dipole) ... negative ion forms

$$H = -\frac{\hbar^2}{2\mu} \nabla^2 + \langle nlm | V_{ed} (\vec{R} - \vec{r}) | nlm \rangle - \frac{\vec{d} \cdot \vec{R}}{R^3}$$

Handwritten notes on a vertical line:

$$\frac{d^2 u}{dx^2} = -\frac{\gamma}{\sinh^2 x} u$$

$u'' = -\frac{\gamma}{x^2} u$ $u = x^l$
 $u = x^l$ $l(l-1) + \gamma = 0$
 $l(l-1) x^{l-2}$

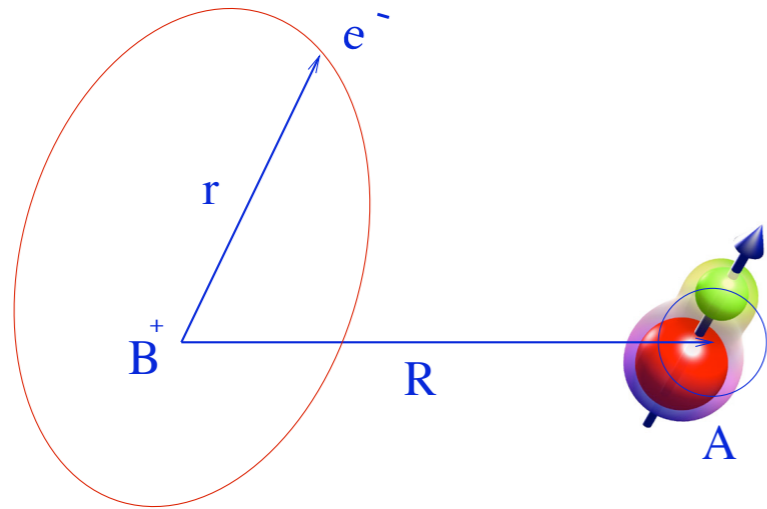
$l^2 - l + \gamma = 0$ $l = \frac{1 \pm \sqrt{1-4\gamma}}{2}$
 $= \frac{1 \pm i\sqrt{4\delta-1}}{2}$

$x^{\frac{1}{2}} e^{\pm \frac{i}{2}\sqrt{4\delta-1} \log x}$

$\gamma < \frac{1}{4}$

Fig. 5. Condition on modified separation constant $\gamma = -\alpha - \epsilon$ for zero-energy solution. Notebook 100 (D12), p. 297.

Switching gear ...



Seth Rittenhouse... (last week)

... no longer short range
scattering length picture does not hold

e^- - dipole interaction:

$$\lambda(\lambda + 1)/R^2 = (a - 1/4)/R^2$$

$a > a_c = 0.639$ a.u. = 1.63 D ... Fermi-Teller dipole

... e^- - binds to dipole (supercritical dipole) ... negative ion forms

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 + \langle nlm | V_{ed}(\vec{R} - \vec{r}) | nlm \rangle - \frac{\vec{d} \cdot \vec{R}}{R^3}$$

- longest range interaction in cold atom physics
- anisotropic interaction

$$\frac{d^2 u}{dx^2} = -\frac{\gamma}{\sinh^2 x} u$$

$$u'' = -\frac{\gamma}{x^2} u \quad u = x^l \quad l(l-1) + \gamma = 0$$

$$u = x^l \quad l(l-1) x^{l-2}$$

$$l^2 - l + \gamma = 0 \quad \left\{ \begin{array}{l} l = \frac{1 \pm \sqrt{1-4\gamma}}{2} \\ = \frac{1 \pm i\sqrt{4\gamma-1}}{2} \end{array} \right.$$

$$x^{\frac{1}{2}} \left[\frac{\pm i}{2} \sqrt{4\gamma-1} \log x \right]$$

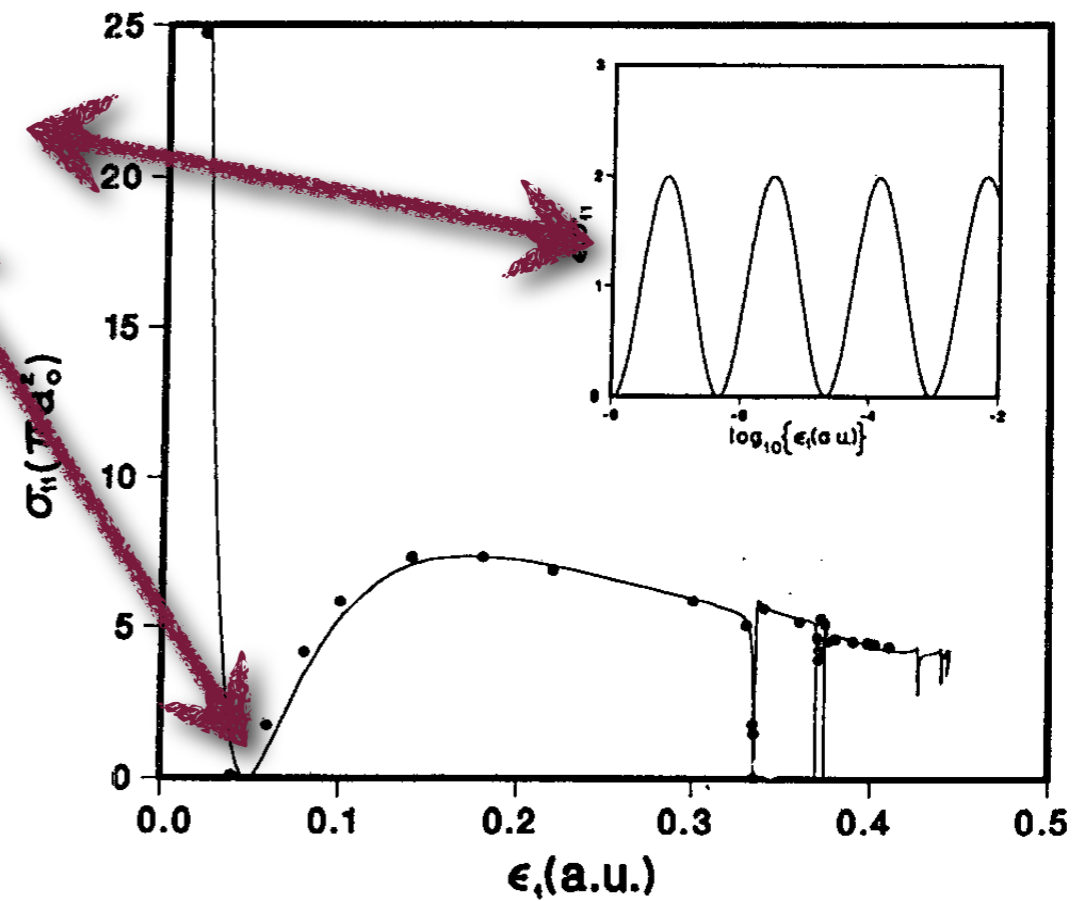
$$\gamma < \frac{1}{4}$$

Fig. 5. Condition on modified separation constant $\gamma = -\alpha - \epsilon$ for zero-energy solution. Notebook 100 (D12), p. 297.

... Of dipole scattering and bound states

$$\phi(k_n, \alpha_n) = \tan^{-1} \left[\frac{\tan[\alpha_n \ln(k_n/2) + \chi_\alpha]}{\tanh(\pi\alpha_n/2)} \right]$$

$$\chi_\alpha = \arg[\Gamma(1 - i\alpha_n)], \quad \alpha_n = (a_n - \frac{1}{4})^{1/2}$$



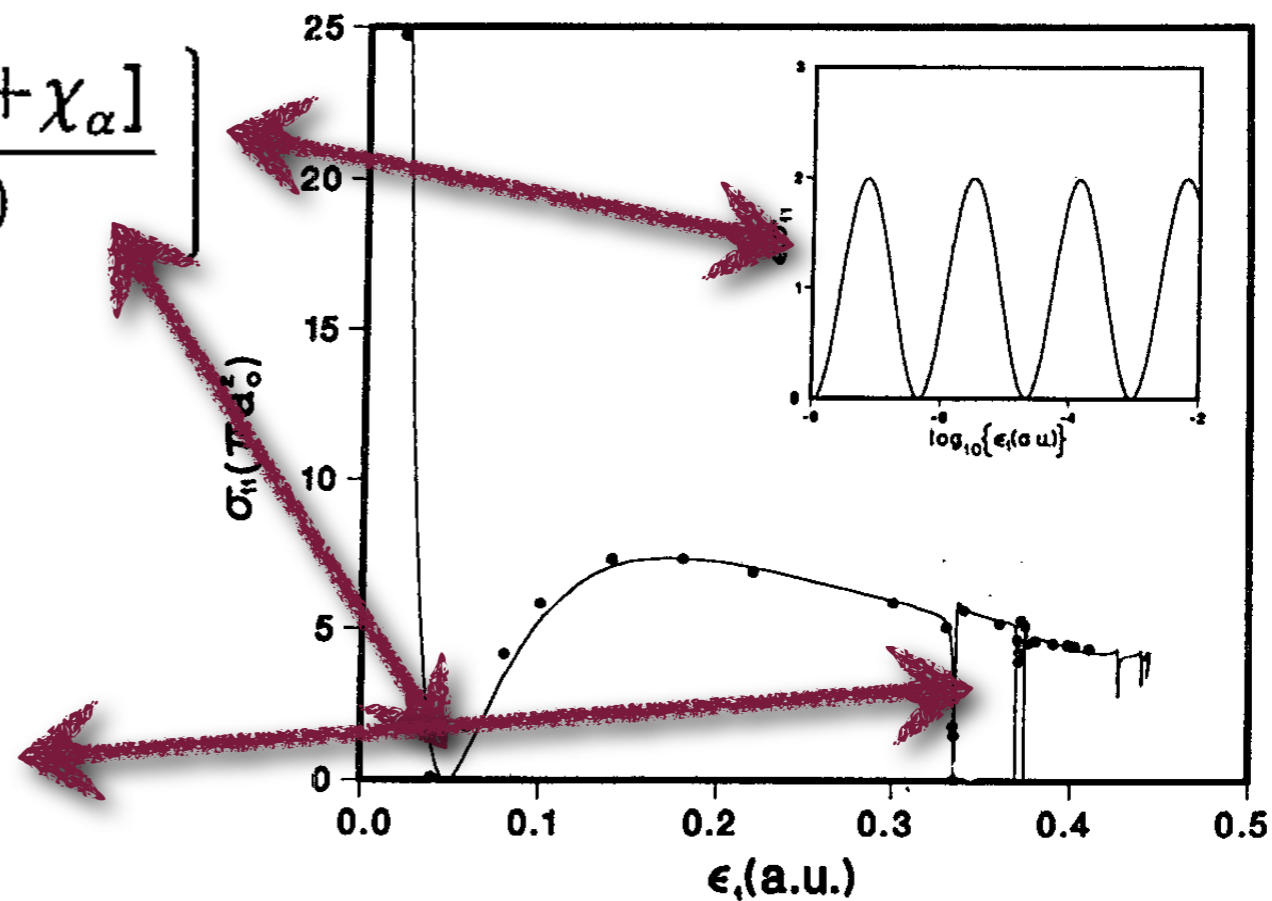
... Of dipole scattering and bound states

$$\phi(k_n, \alpha_n) = \tan^{-1} \left[\frac{\tan[\alpha_n \ln(k_n/2) + \chi_\alpha]}{\tanh(\pi\alpha_n/2)} \right]$$

$$\chi_\alpha = \arg[\Gamma(1 - i\alpha_n)], \quad \alpha_n = (a_n - \frac{1}{4})^{1/2}$$

Exponential convergence of bound states

$$\epsilon^{(m)} = \epsilon^{(0)} \exp(-2m\pi/\alpha)$$



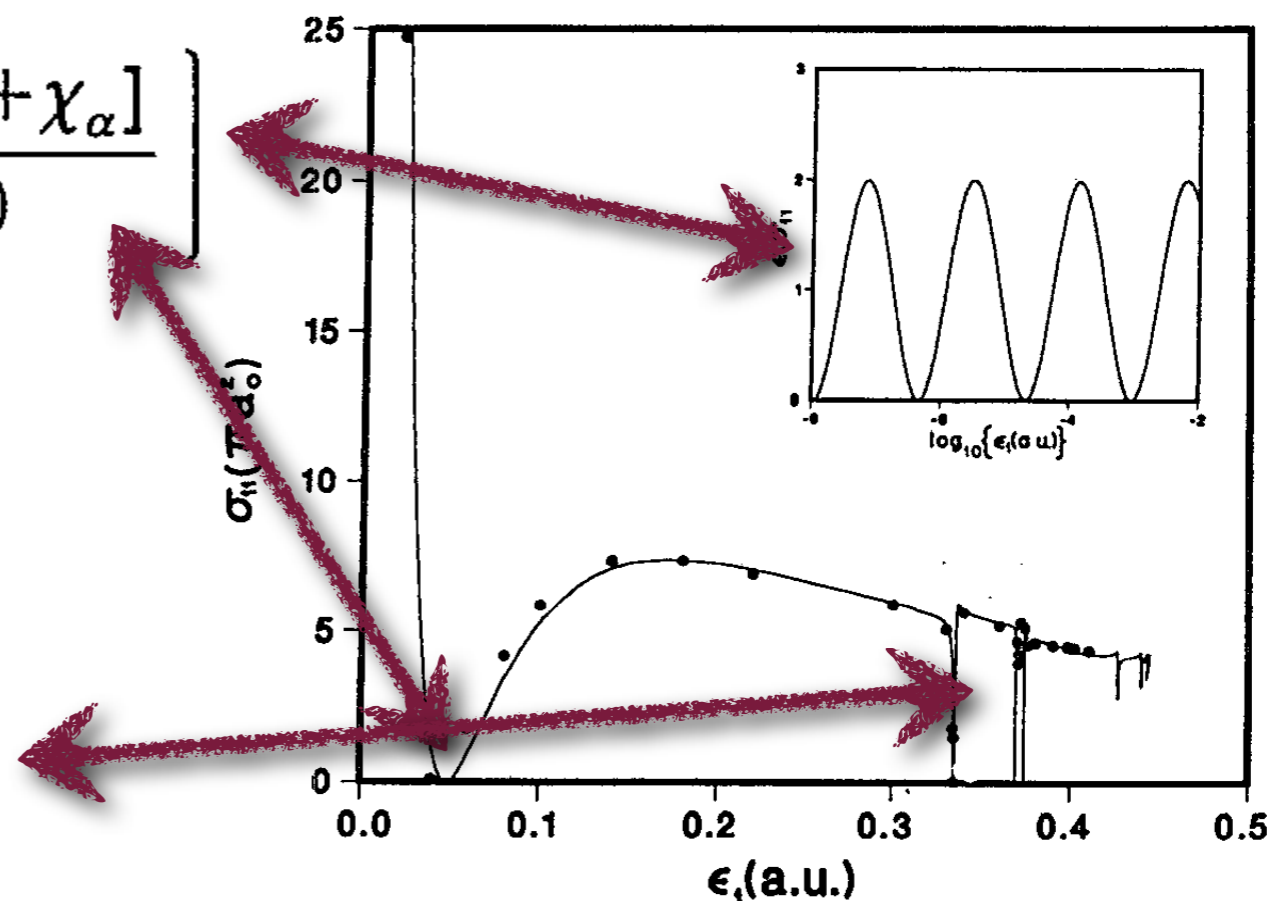
... Of dipole scattering and bound states

$$\phi(k_n, \alpha_n) = \tan^{-1} \left[\frac{\tan[\alpha_n \ln(k_n/2) + \chi_\alpha]}{\tanh(\pi\alpha_n/2)} \right]$$

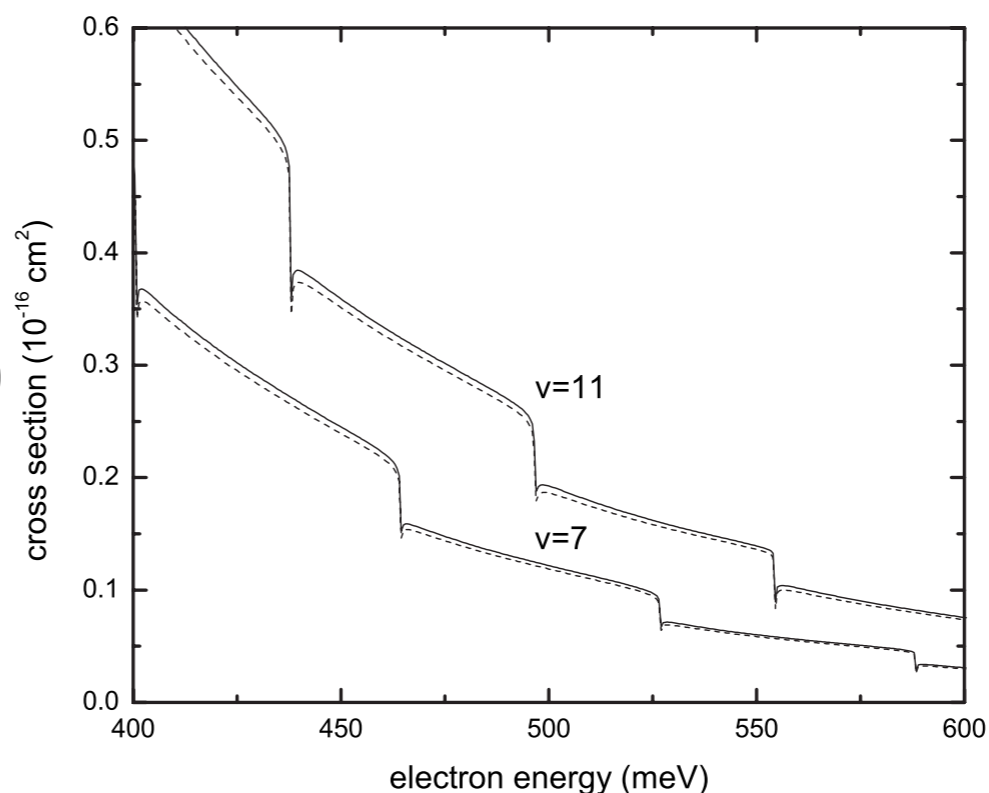
$$\chi_\alpha = \arg[\Gamma(1 - i\alpha_n)], \quad \alpha_n = (a_n - \frac{1}{4})^{1/2}$$

Exponential convergence of bound states

$$\epsilon^{(m)} = \epsilon^{(0)} \exp(-2m\pi/\alpha)$$



Dissociative electron attachment to CH_3Br
(Gallup + Fabrikant 2007)



... large two-body scattering length (no binding)

... Entirely different physics, but with the same long-range interaction... Efimov physics

$$a/R^2 \quad \epsilon^{(m)} = \epsilon^{(0)} \exp(-2m\pi/s_0) \quad s_0=1.0062378$$

... large two-body scattering length (no binding)

Universality of few-body physics ... large two-body interactions and few-body binding

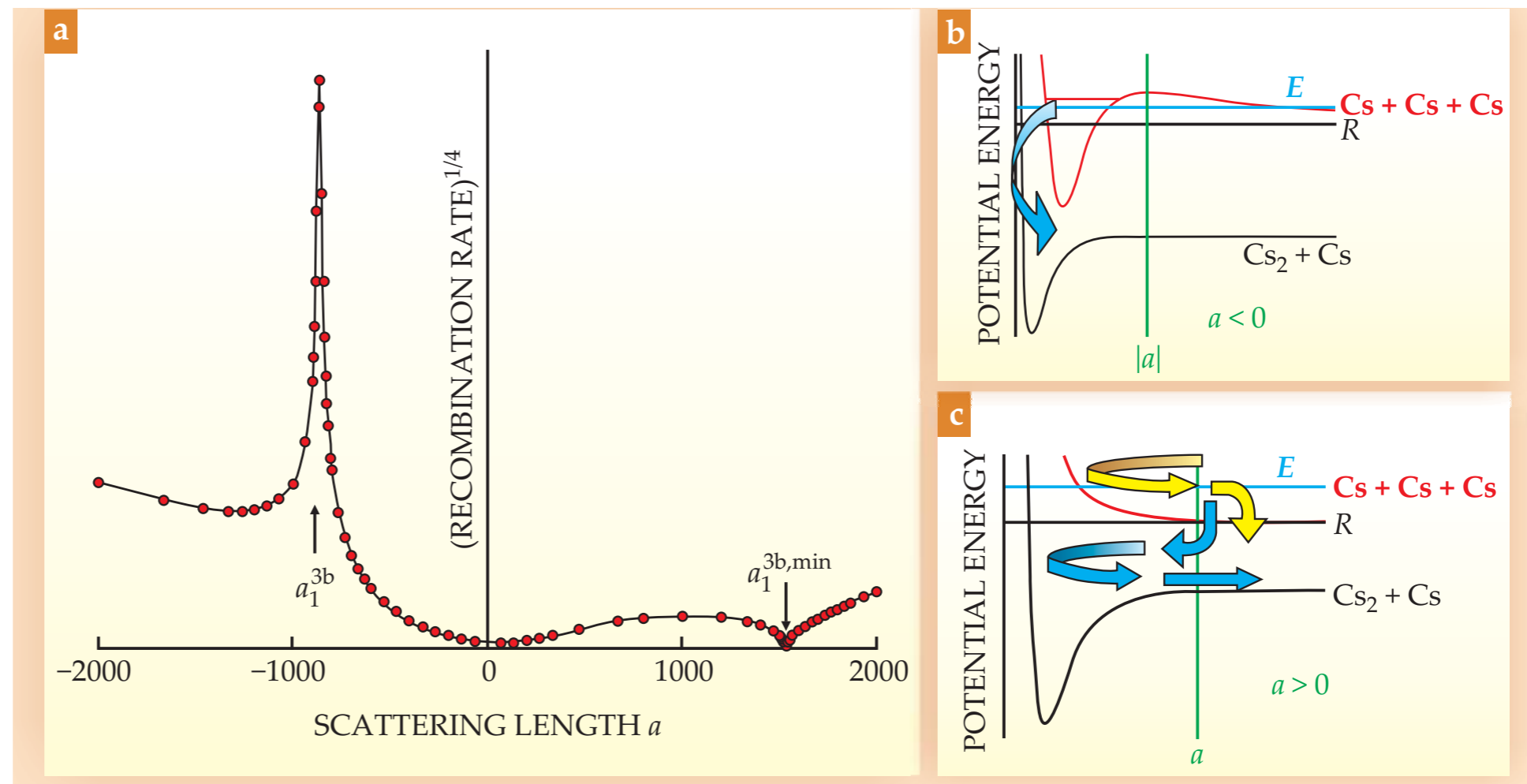
... Entirely different physics, but with the same long-range interaction... Efimov physics

$$a/R^2 \quad \epsilon^{(m)} = \epsilon^{(0)} \exp(-2m\pi/s_0) \quad s_0=1.0062378$$

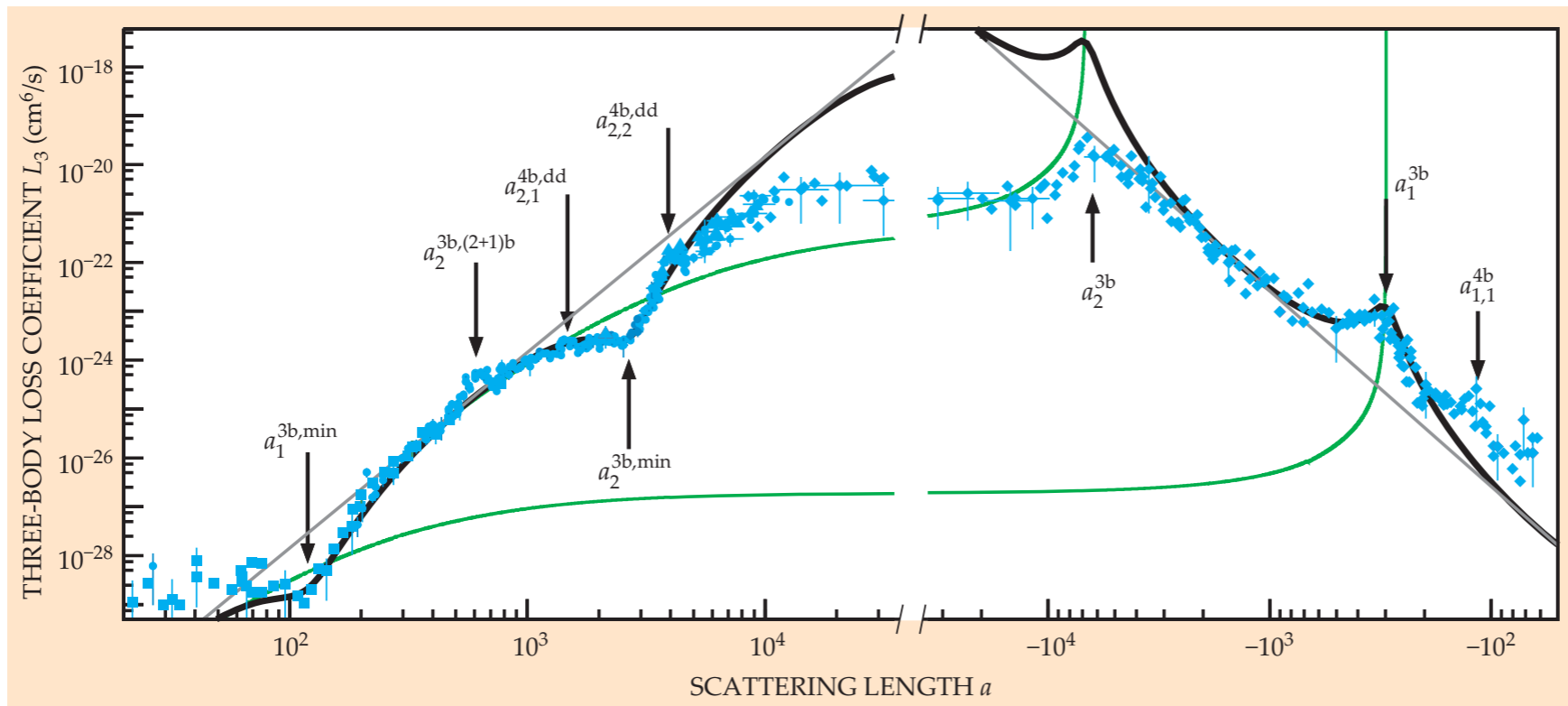
... large two-body scattering length (no binding)

Universality of few-body physics ... large two-body interactions and few-body binding

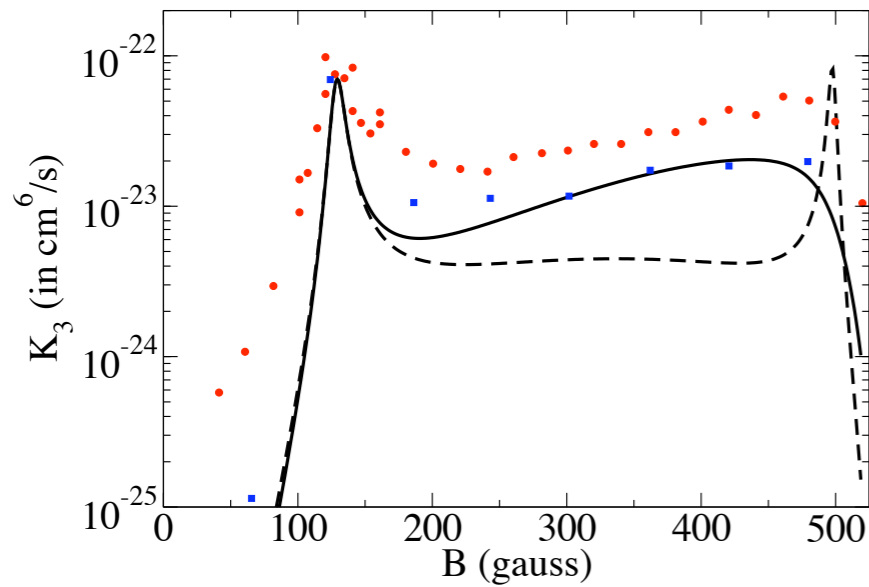
Greene, Nat. Phys. (2009)
and Phys. Today (2010)



Hulet et al, Science (2009)

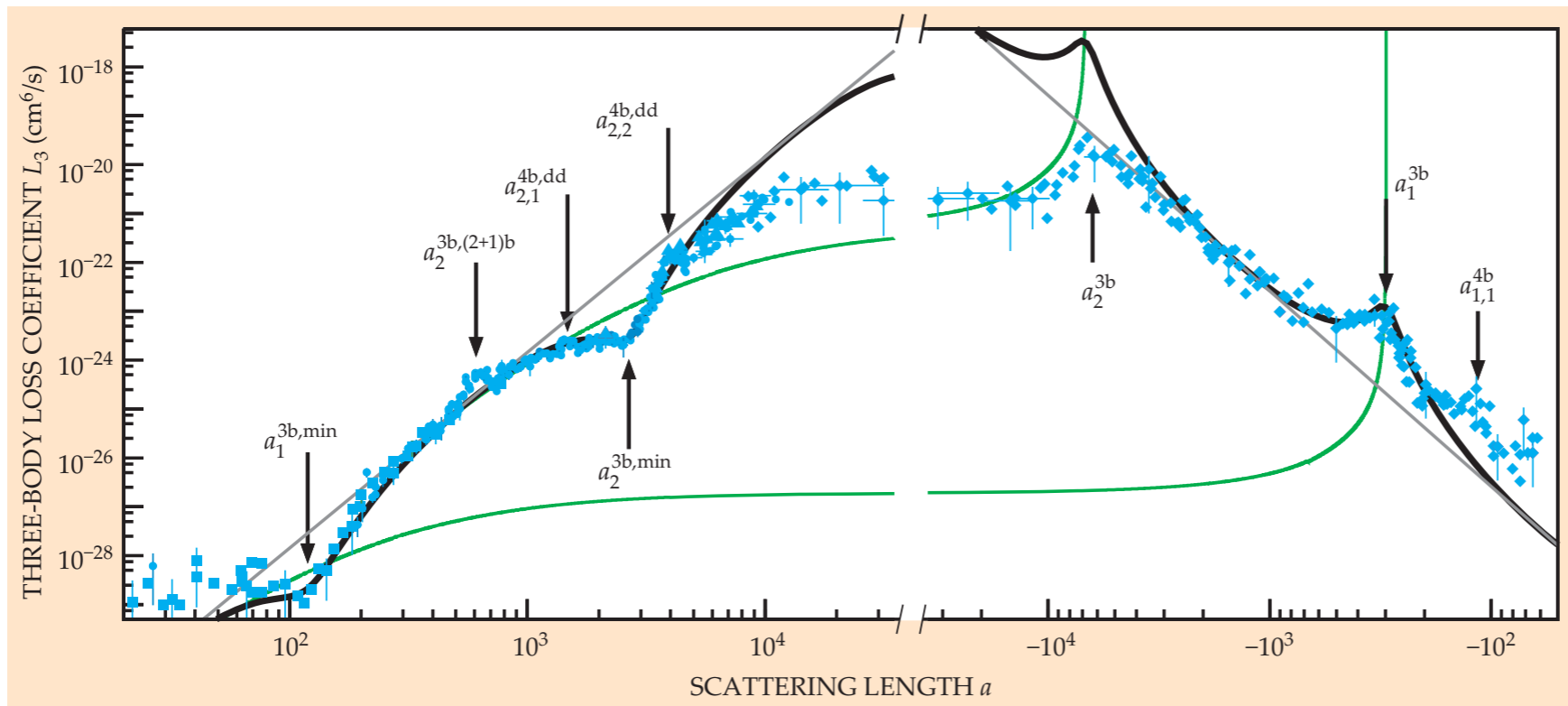


Rittenhouse (2010)

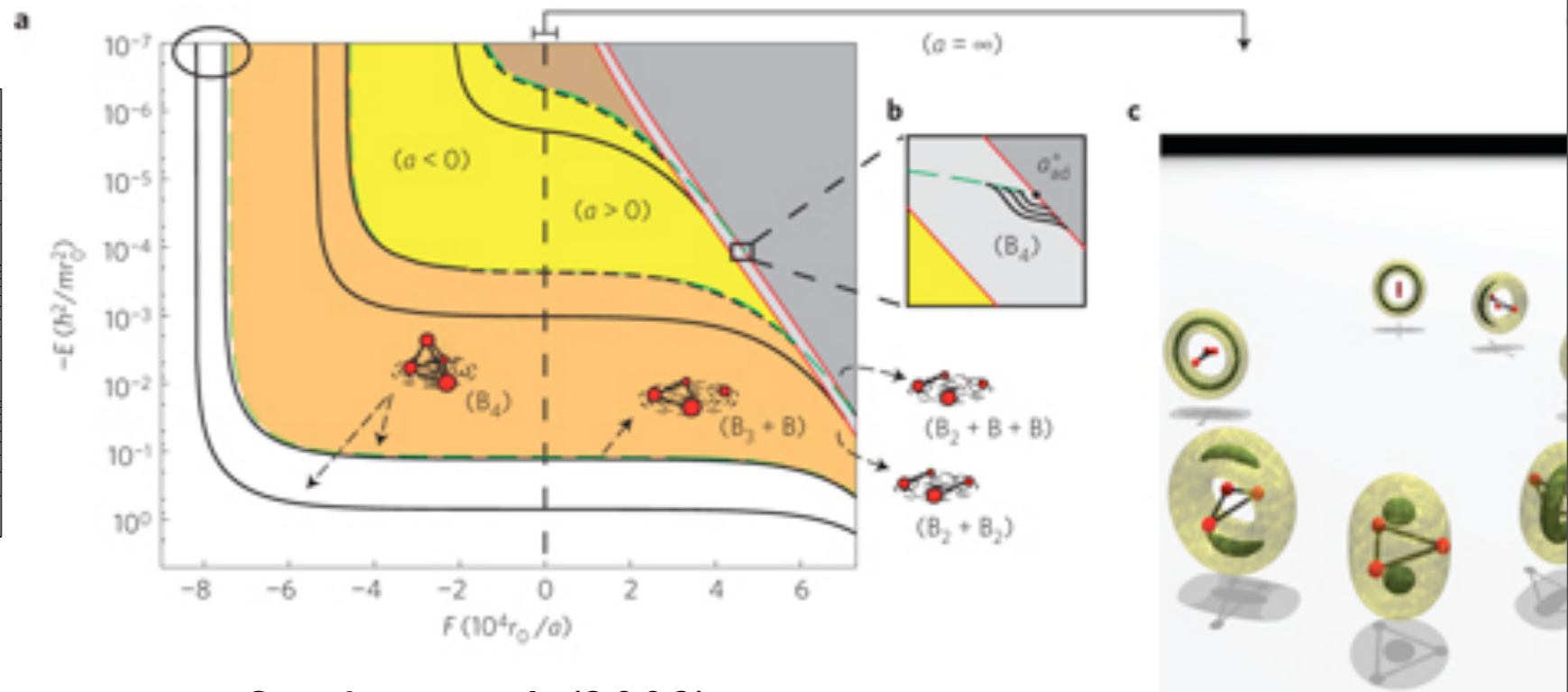
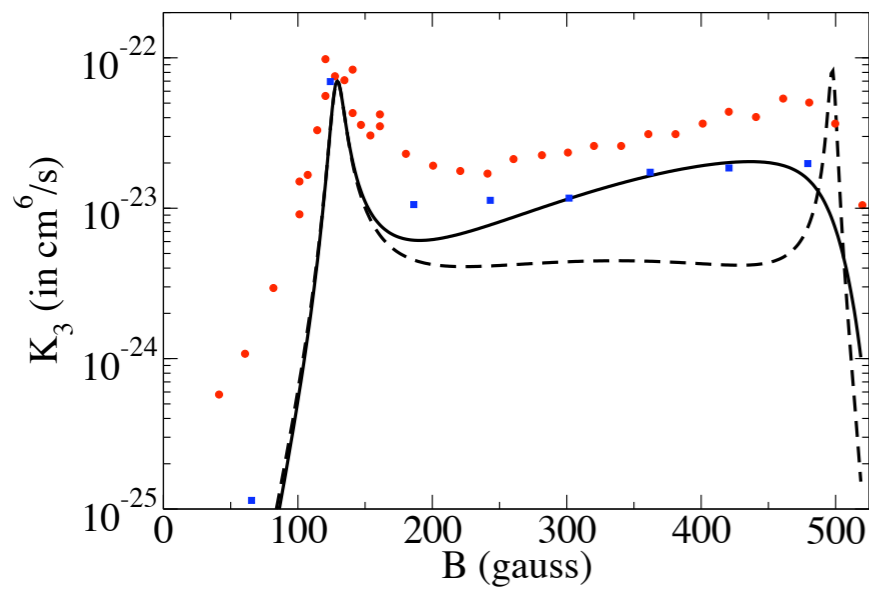


von Stecher et al. (2009)

Hulet et al, Science (2009)



Rittenhouse (2010)



von Stecher et al. (2009)

Λ – *doublet* molecules (OH, CH)

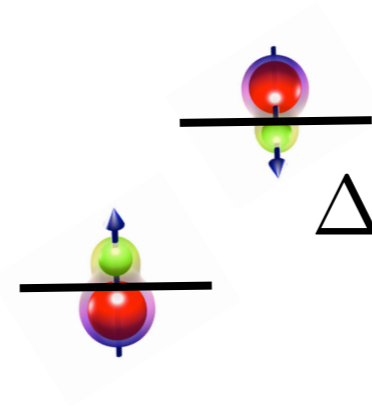
molecules with small rotational constants (KRb, RbCs)

Λ – *doublet* molecules (OH, CH)

molecules with small rotational constants (KRb, RbCs)

two-level system

$$H_{\Lambda} = \begin{pmatrix} -Q & -\Delta/2 \\ -\Delta/2 & Q \end{pmatrix}$$

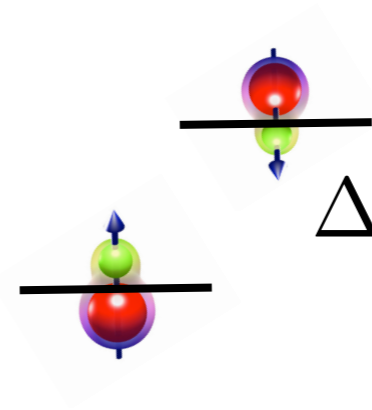


Λ – *doublet* molecules (OH, CH)

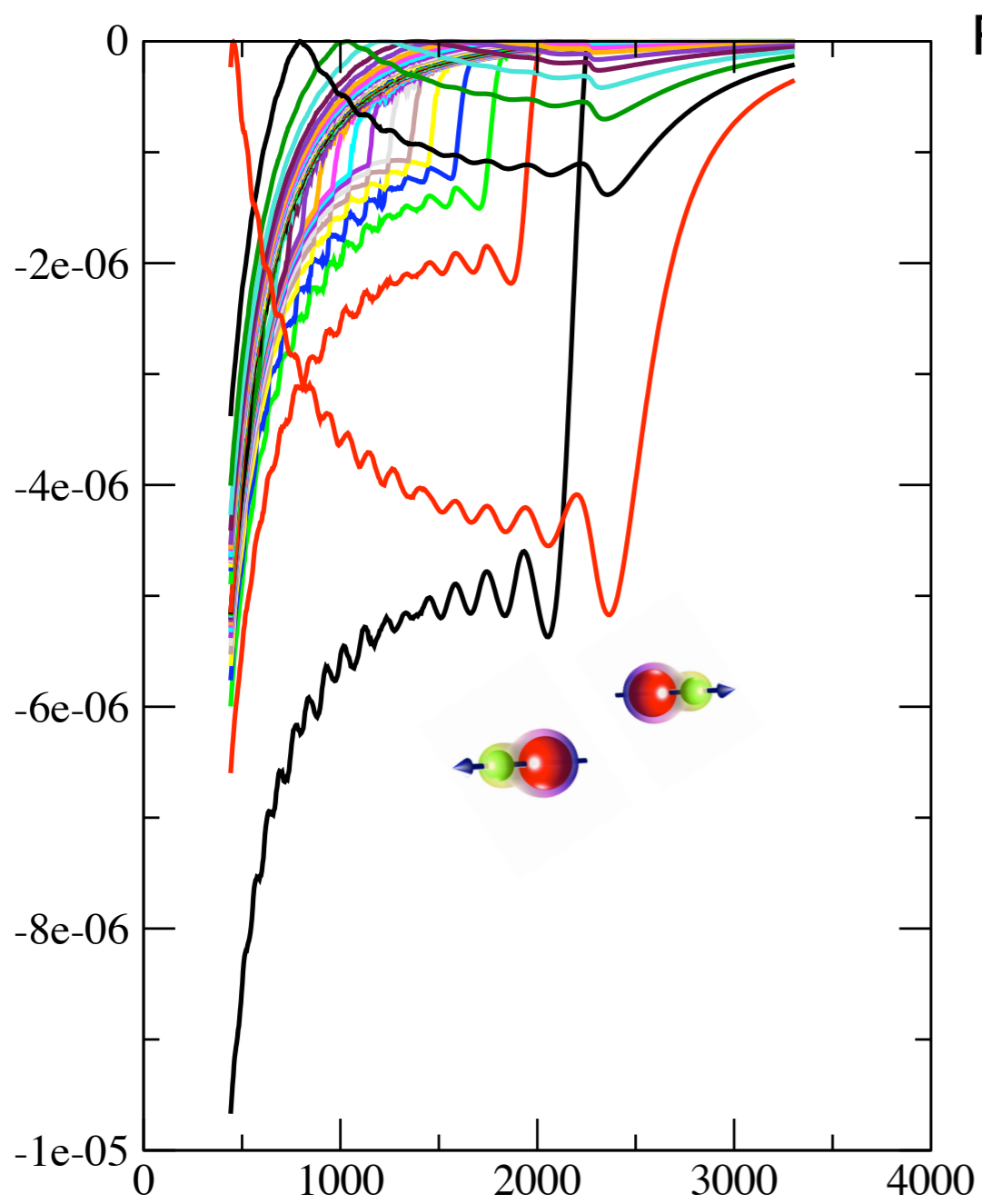
molecules with small rotational constants (KRb, RbCs)

two-level system

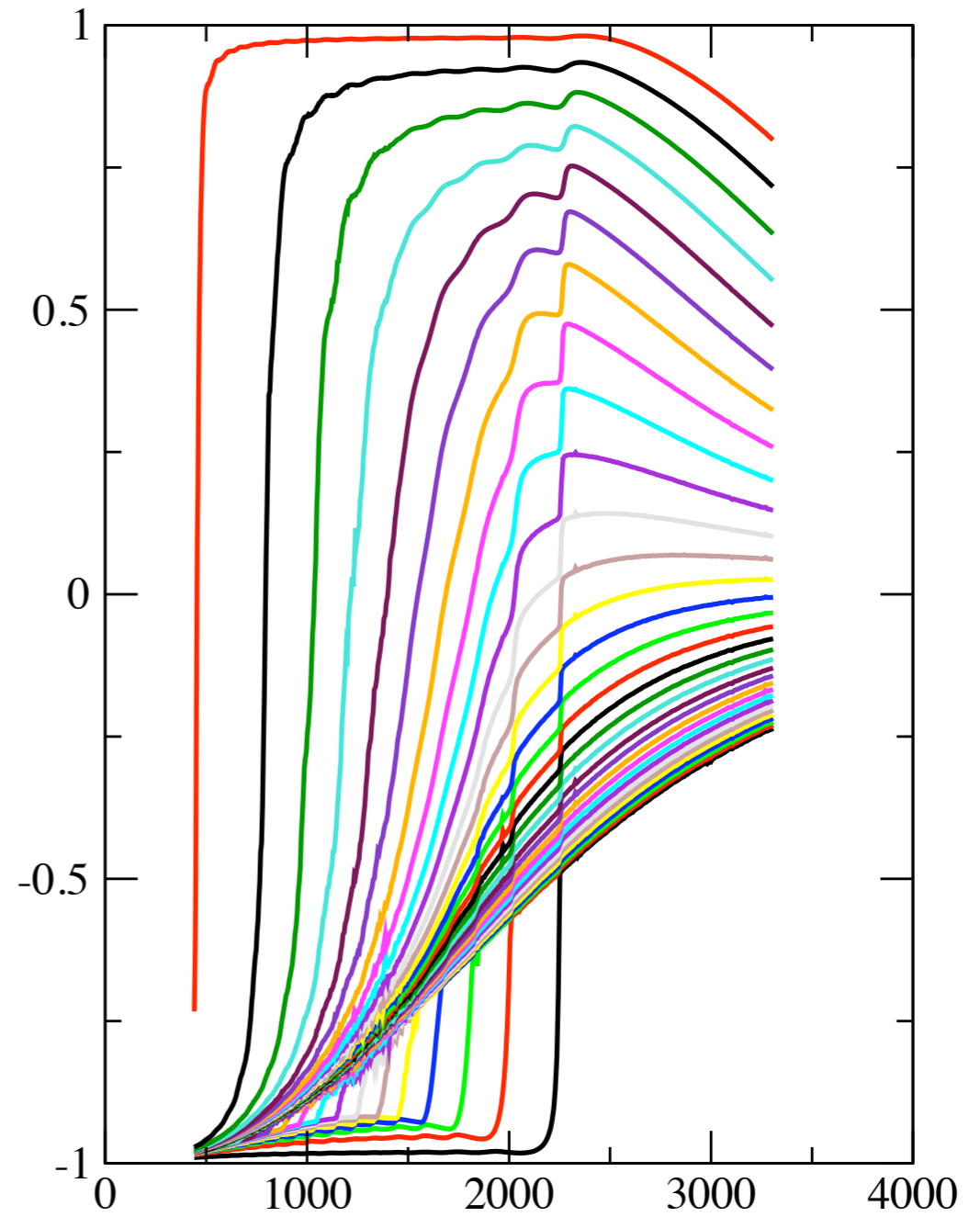
$$H_{\Lambda} = \begin{pmatrix} -Q & -\Delta/2 \\ -\Delta/2 & Q \end{pmatrix}$$



$$V_{\lambda}(R) = d \left[E_c - \sqrt{\left(E_{\lambda}(R) - \frac{1}{R^2} \right)^2 + E_c^2} \right]$$



Rb(n=35)

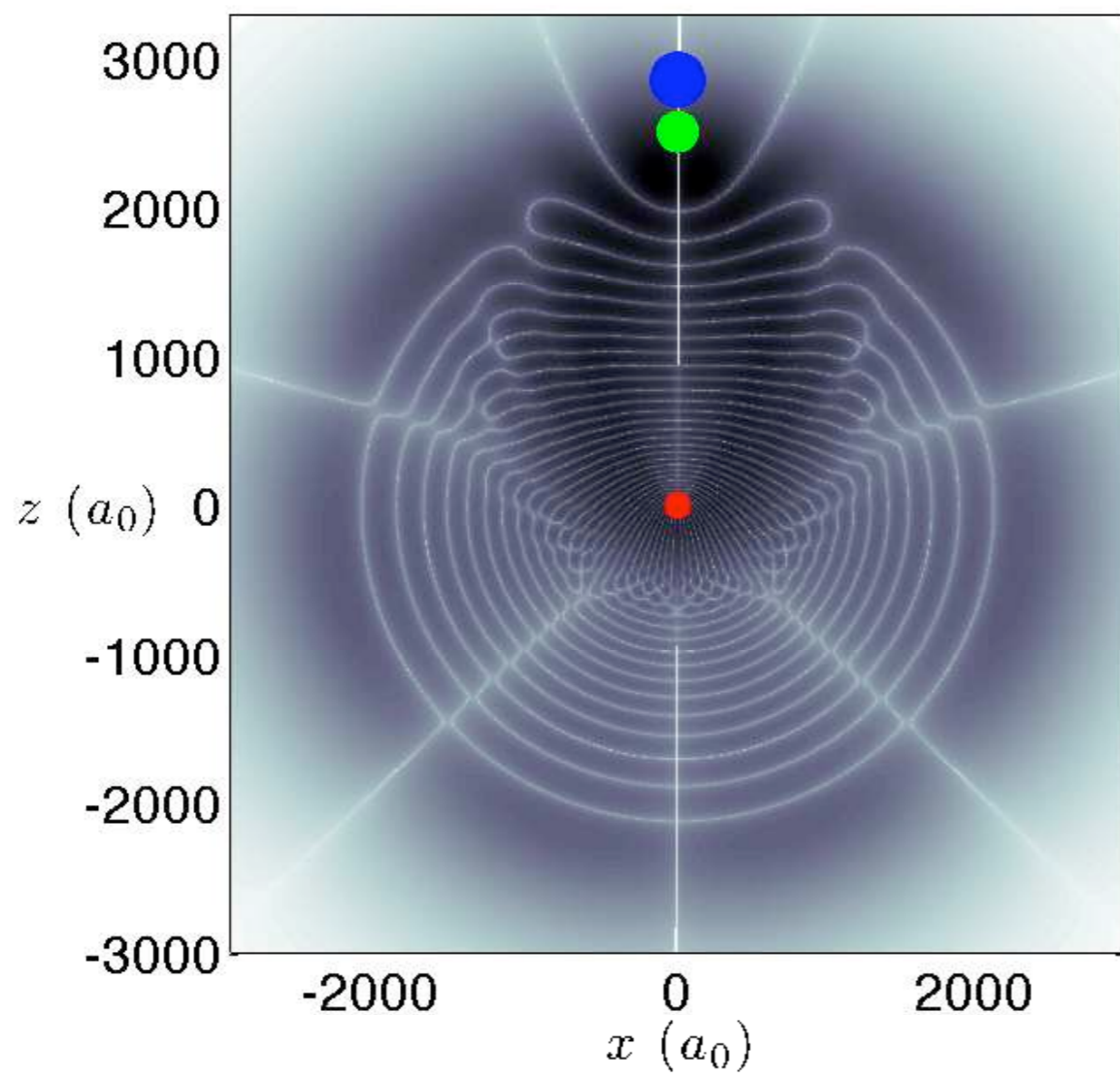


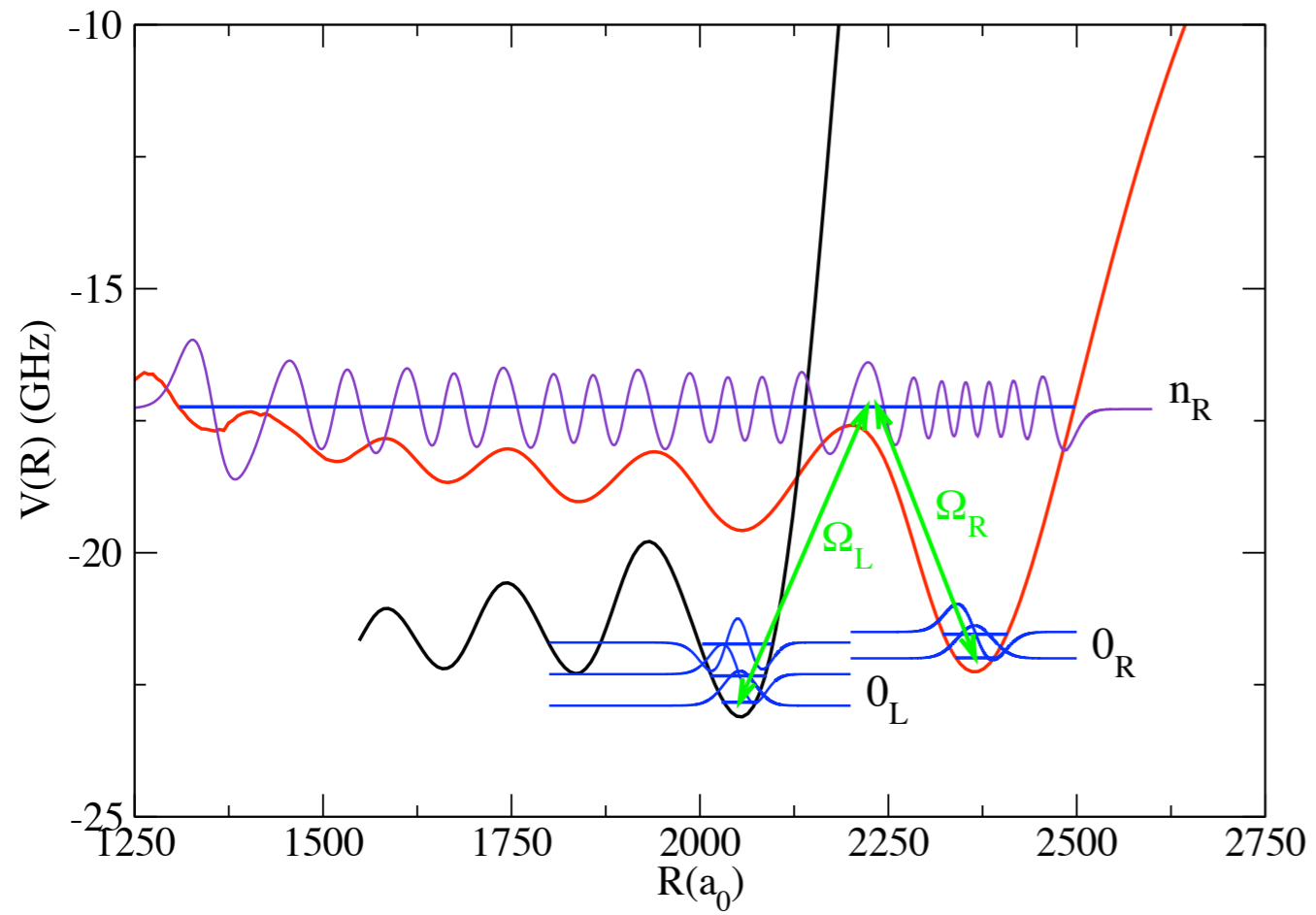
$E_c = 10^{-7} a.u. \sim 500V/cm$

Rittenhouse & Sadeghpour, PRL 2010

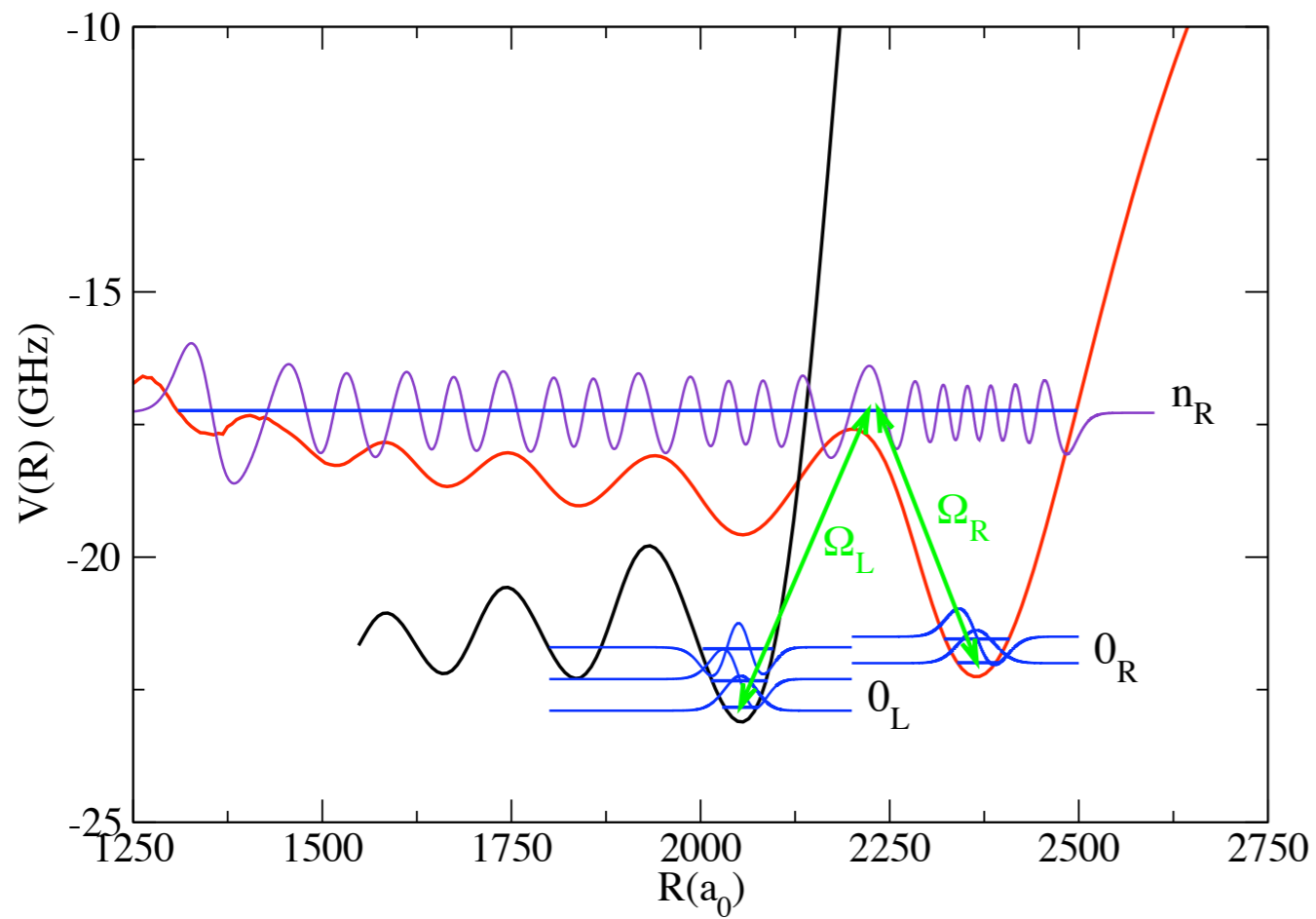
non-adiabatic terms

$$\langle \lambda_2 | \left| \frac{\partial}{\partial R} \lambda_1 (R) \right\rangle = \sum_{l,l'} \langle nl'm | |nlm\rangle a_{nl'm}^{\lambda_2^*} (R) a_{nlm}^{\lambda_1'} (R)$$

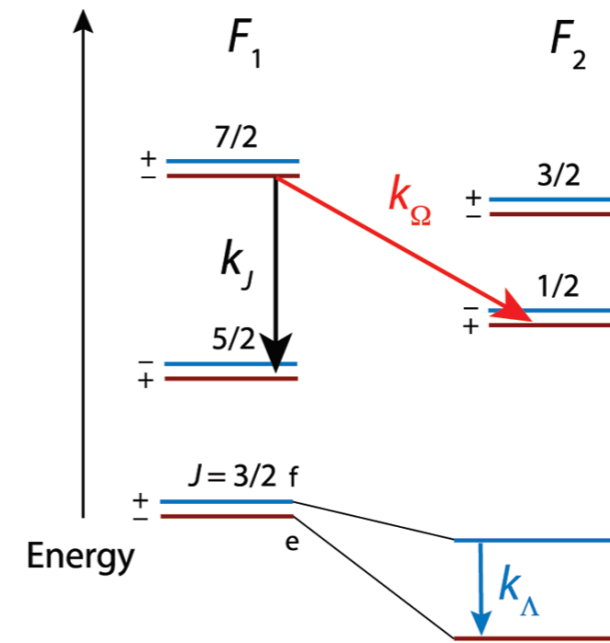
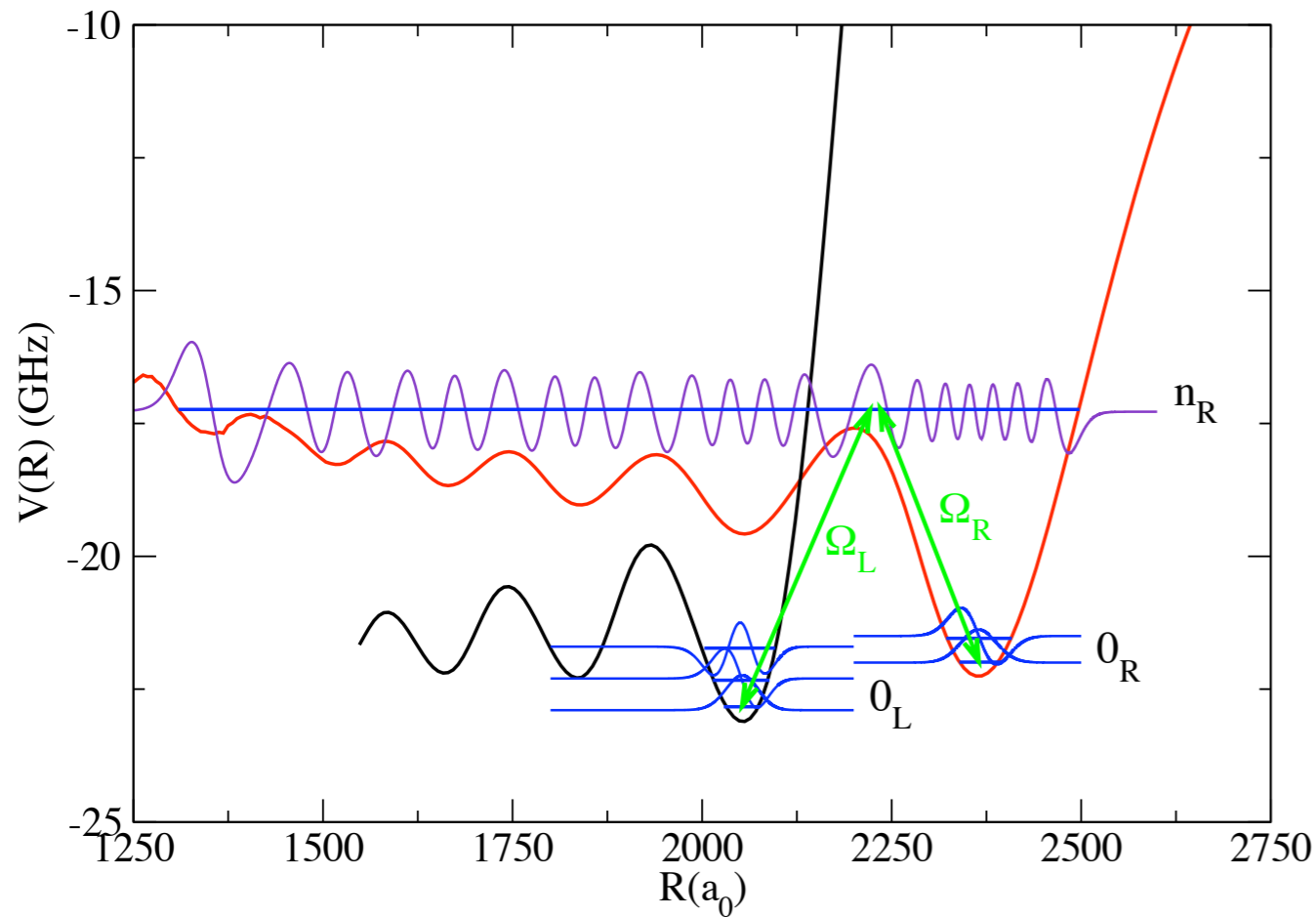




Coherent control of molecular orientation

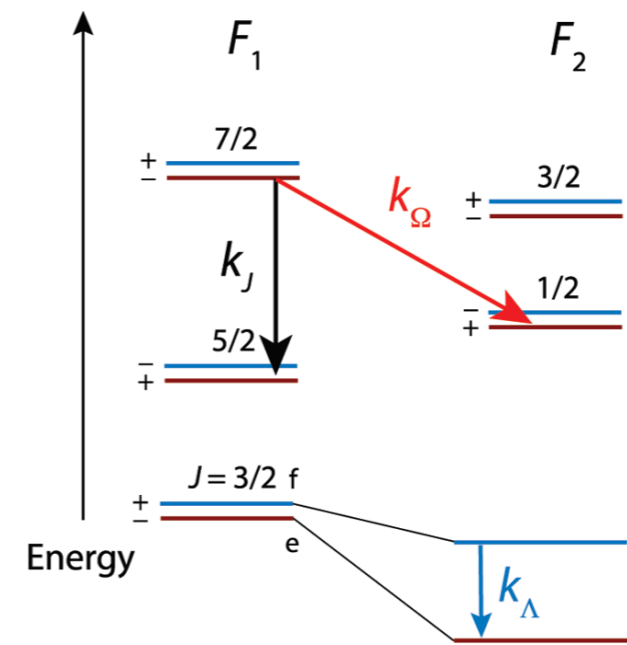
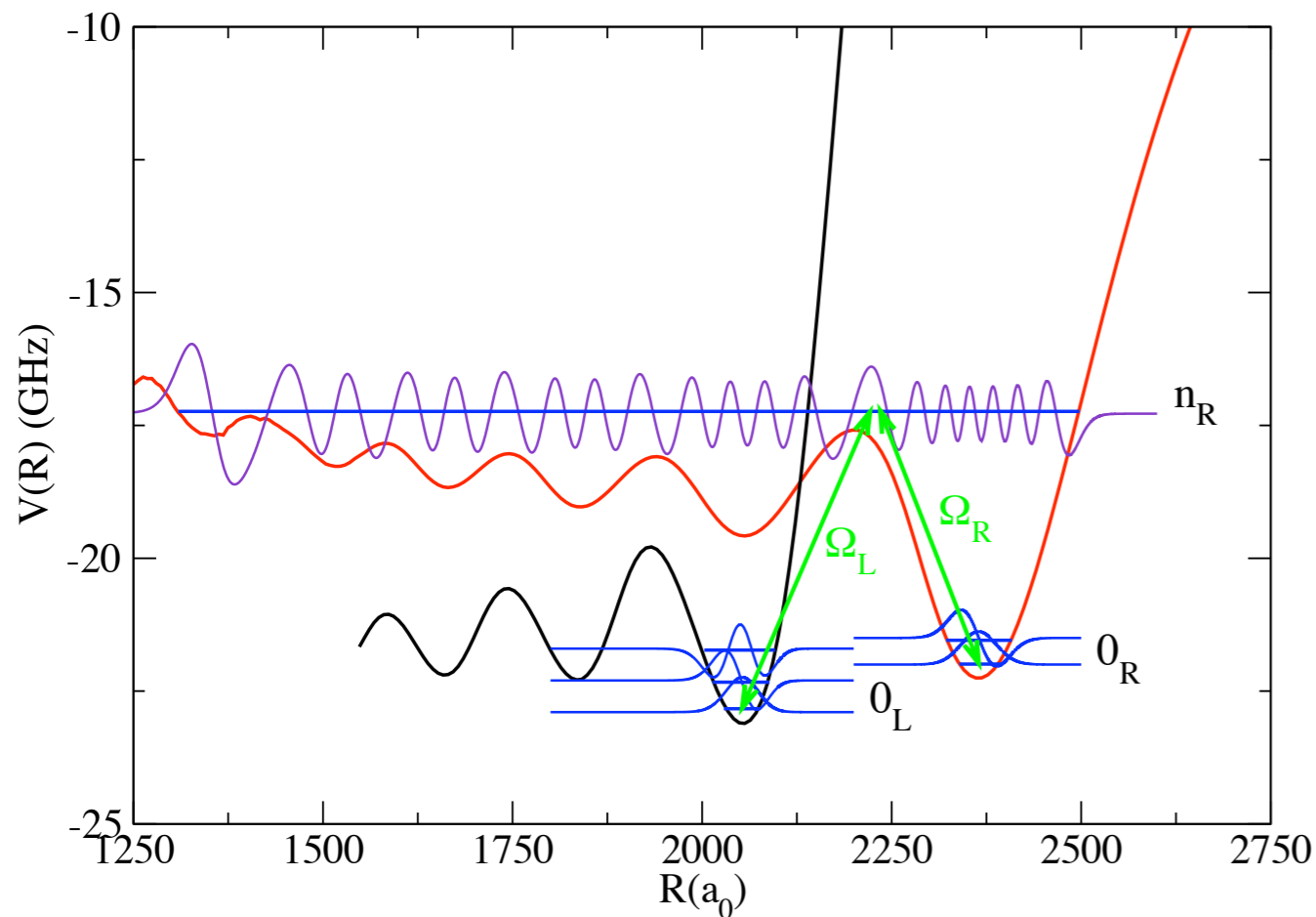


Coherent control of molecular orientation



on-resonance coherent Raman transition

Coherent control of molecular orientation



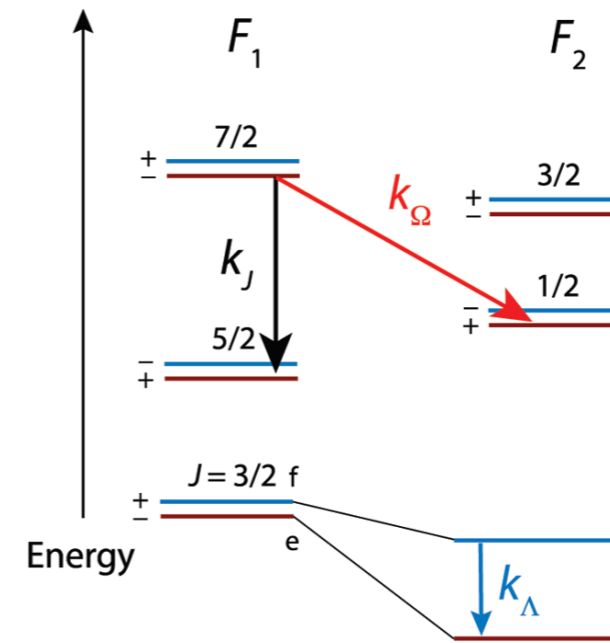
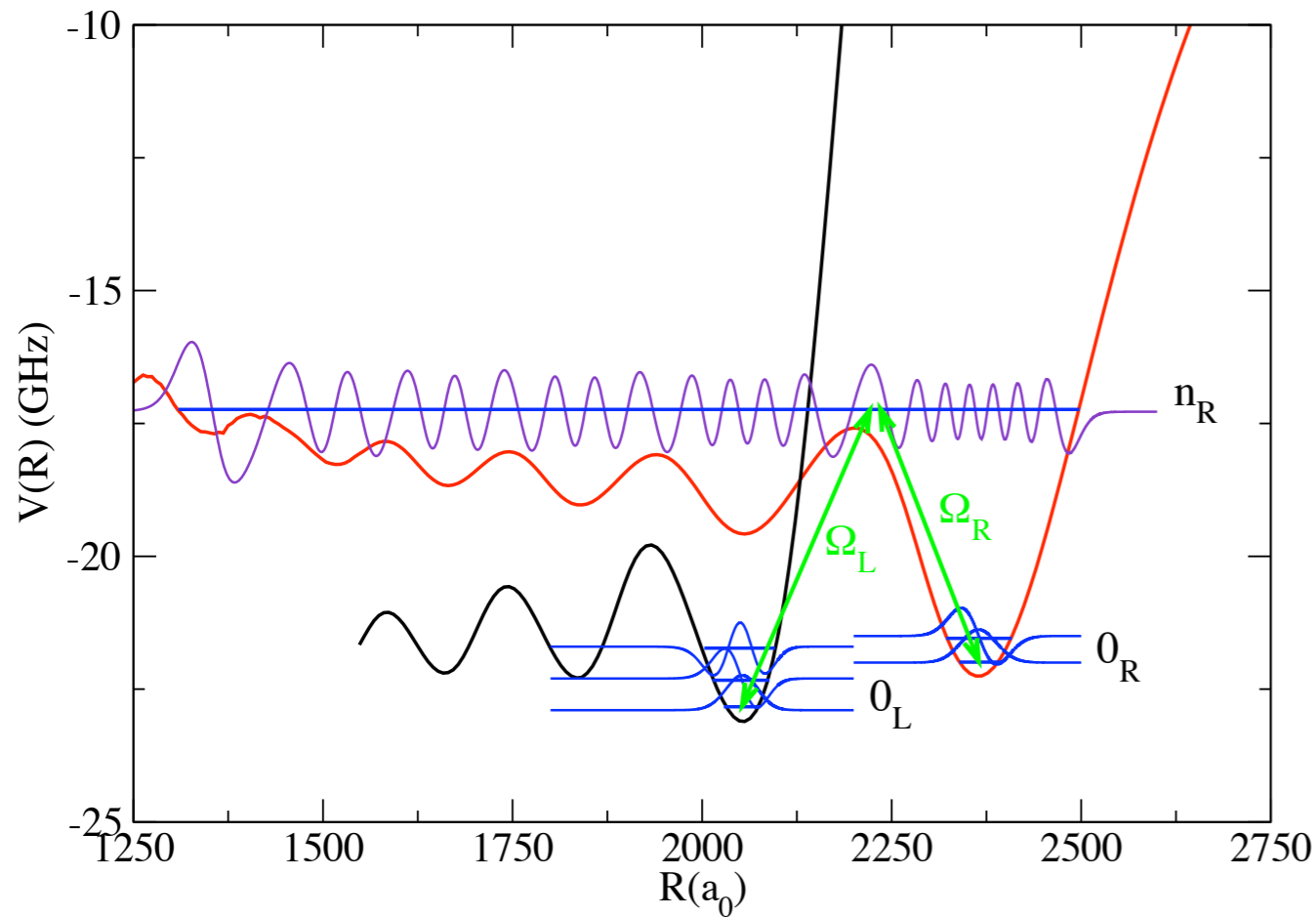
OH:

$$\Delta_\Lambda = 1.7 \text{ GHz}$$

$$d = 1.68D$$

on-resonance coherent Raman transition

Coherent control of molecular orientation



OH:

$$\Delta_\Lambda = 1.7 \text{ GHz}$$

$$d = 1.68D$$

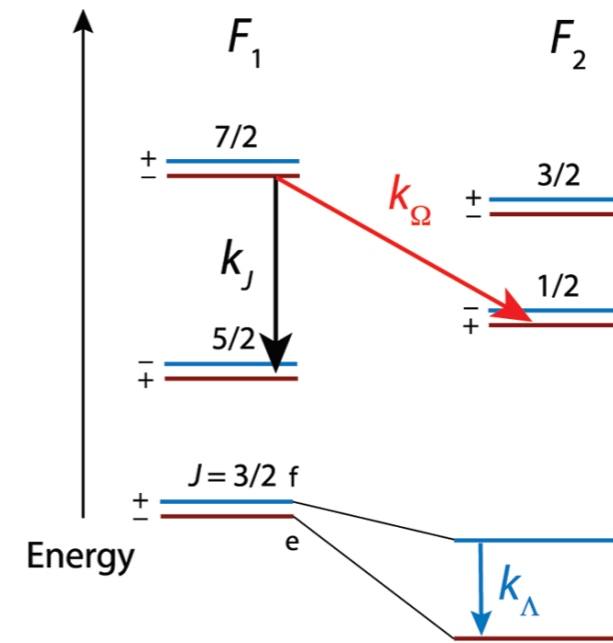
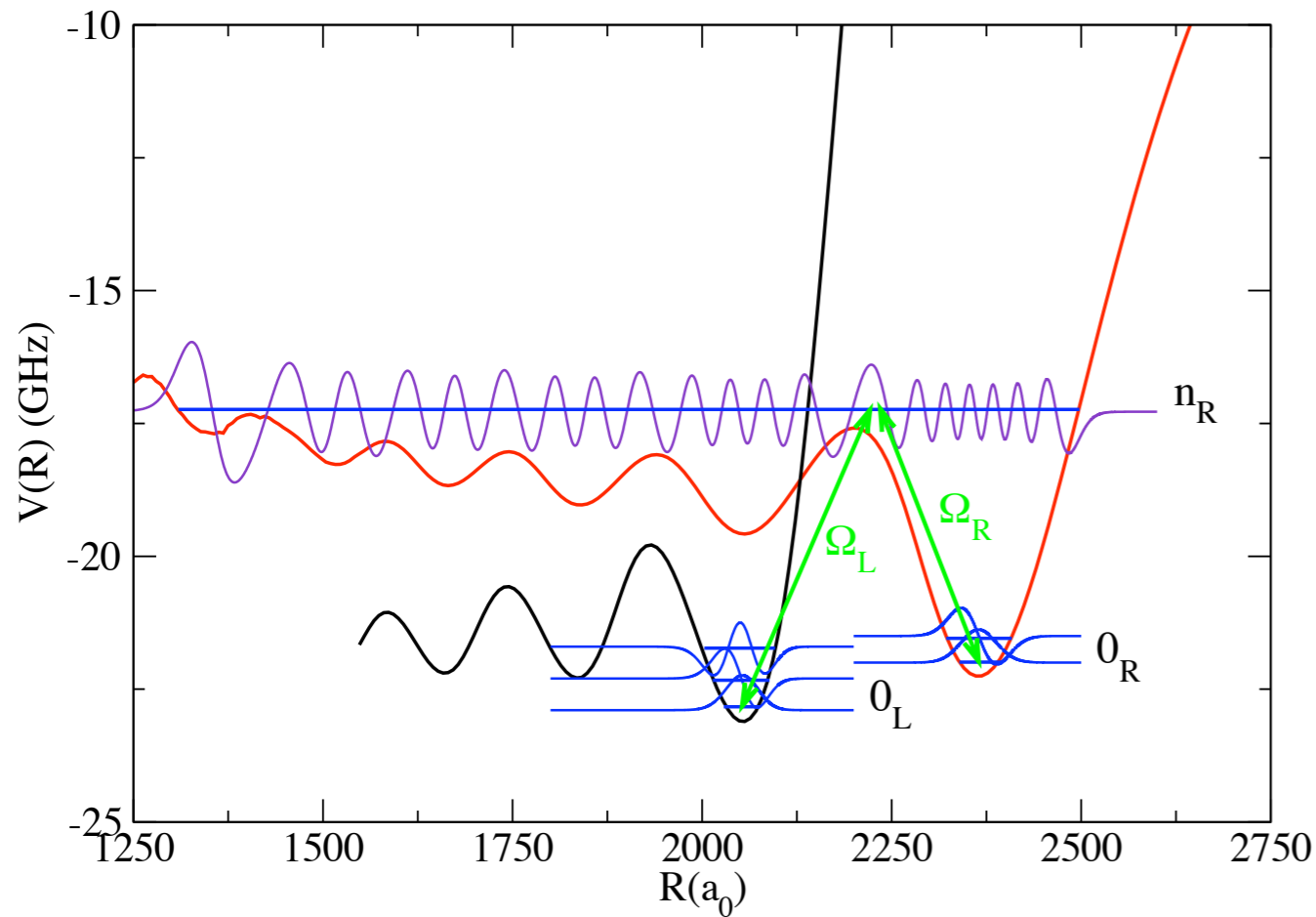
CH:

$$\Delta_\Lambda = 3.03 \text{ GHz}$$

$$d = 1.46D$$

on-resonance coherent Raman transition

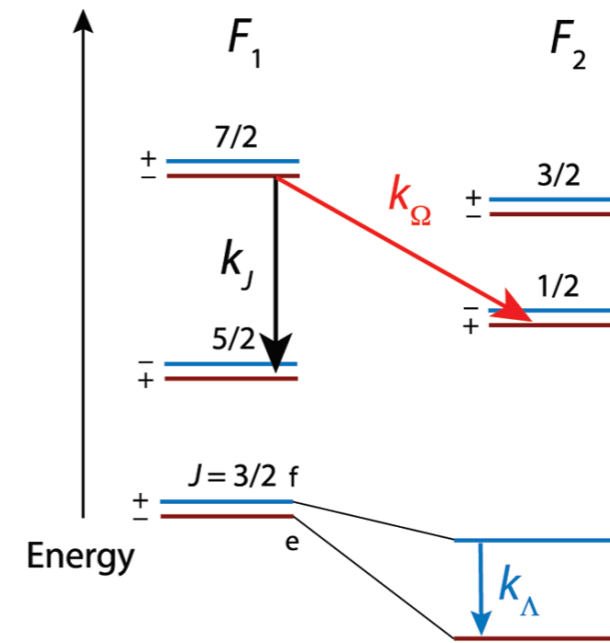
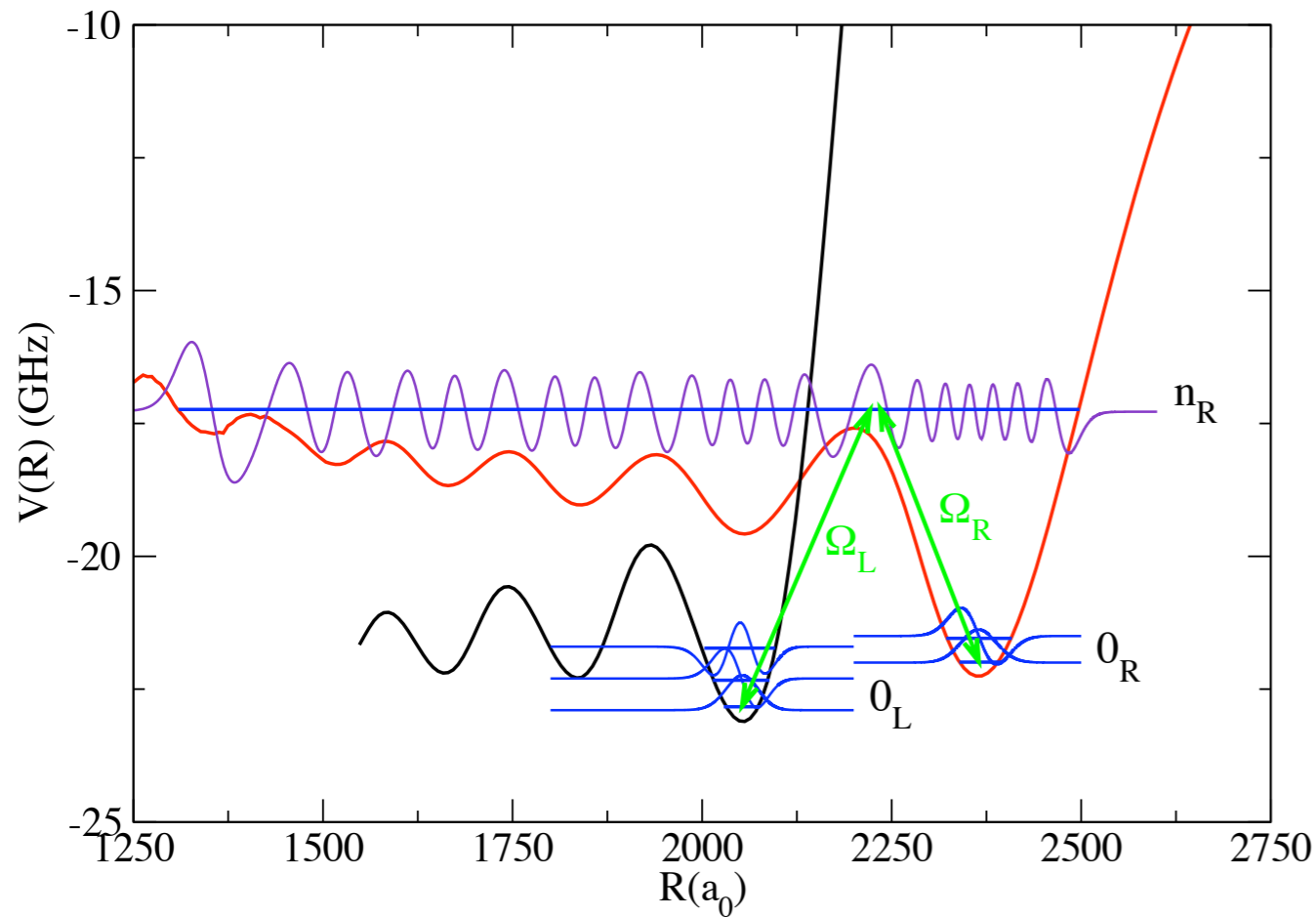
Coherent control of molecular orientation



- OH:** $\Delta_\Lambda = 1.7$ GHz
 $d = 1.68D$
- CH:** $\Delta_\Lambda = 3.03$ GHz
 $d = 1.46D$
- OD:** $\Delta_\Lambda = 0.5$ GHz
 $d = 1.60D$

on-resonance coherent Raman transition

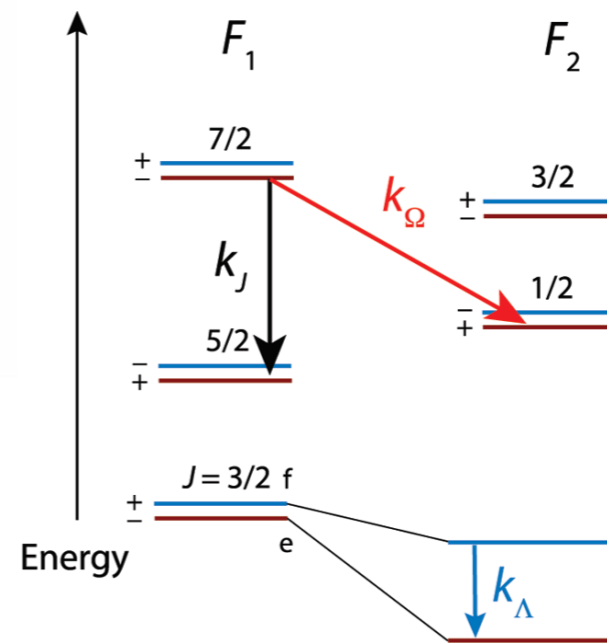
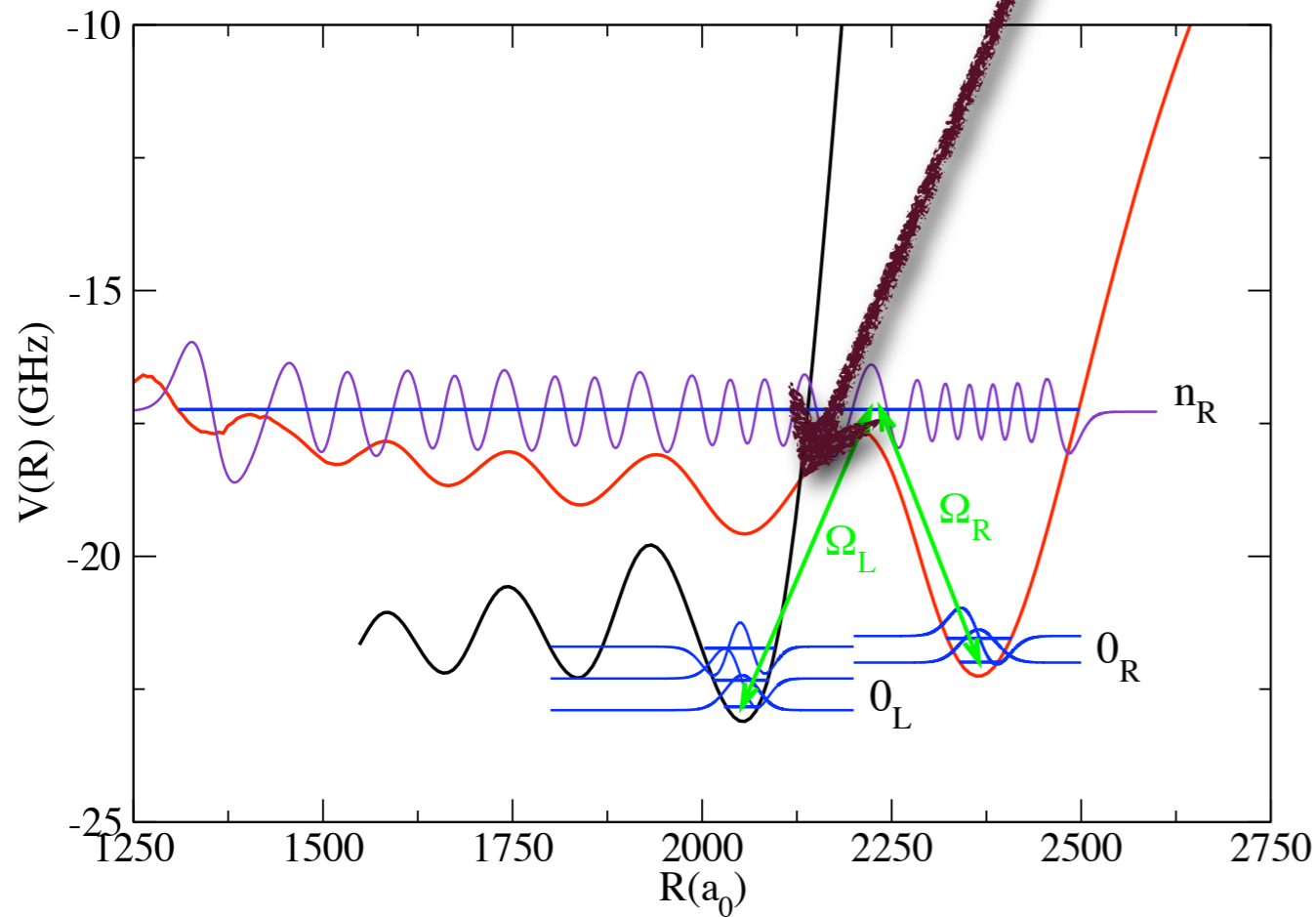
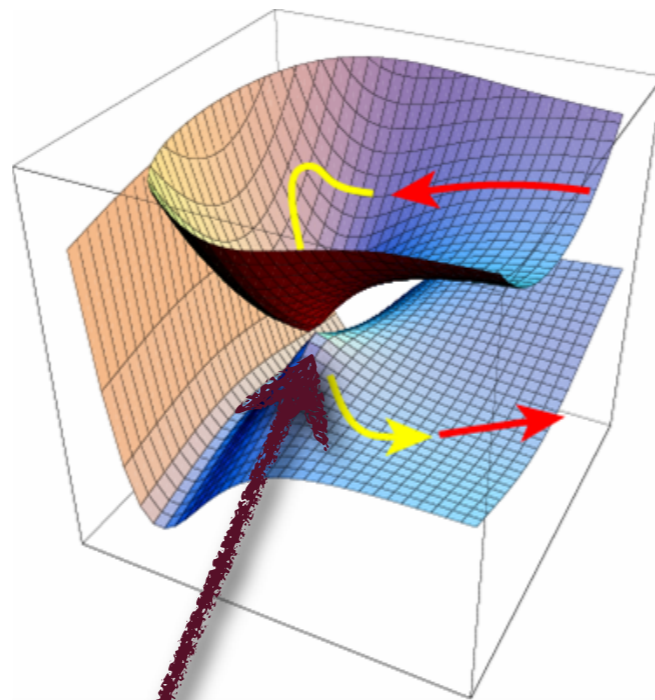
Coherent control of molecular orientation



- OH:** $\Delta_\Lambda = 1.7 \text{ GHz}$
 $d = 1.68D$
- CH:** $\Delta_\Lambda = 3.03 \text{ GHz}$
 $d = 1.46D$
- OD:** $\Delta_\Lambda = 0.5 \text{ GHz}$
 $d = 1.60D$
- CD:** $\Delta_\Lambda = 1.22 \text{ GHz}$
 $d = 1.46D$

on-resonance coherent Raman transition

Coherent control of molecular orientation



- OH:** $\Delta_{\Lambda} = 1.7 \text{ GHz}$
 $d = 1.68D$
- CH:** $\Delta_{\Lambda} = 3.03 \text{ GHz}$
 $d = 1.46D$
- OD:** $\Delta_{\Lambda} = 0.5 \text{ GHz}$
 $d = 1.60D$
- CD:** $\Delta_{\Lambda} = 1.22 \text{ GHz}$
 $d = 1.46D$

on-resonance coherent Raman transition

Higher angular momentum molecules are now accessible

Four-horsemen of chemical bonds: (ionic, covalent, hydrogen, and van der Waals)

... may now have company; ultralong Rydberg bond

