

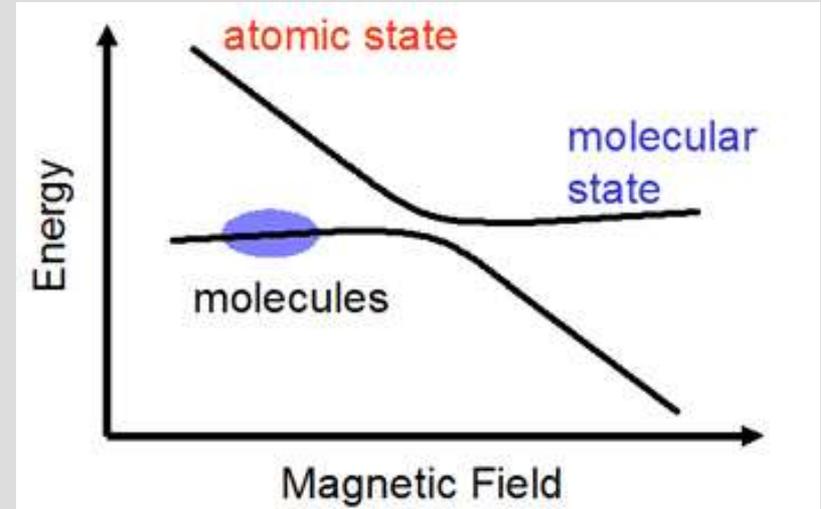
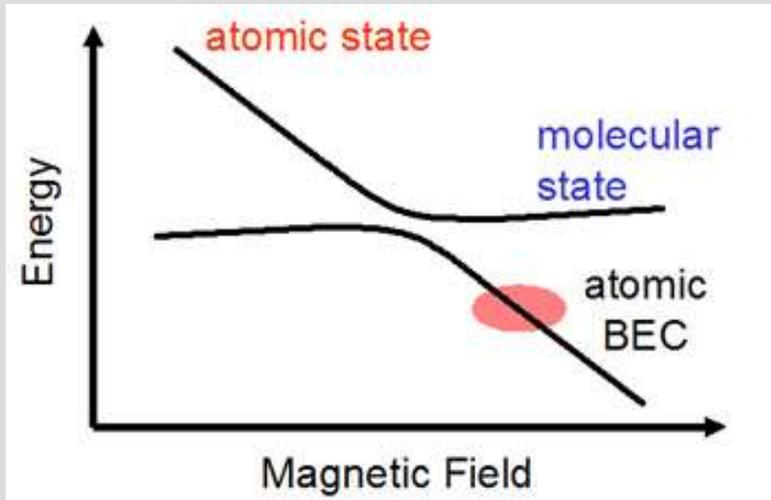
Molecules with electric and magnetic dipoles:
magnetoassociation of alkali-metal with closed-shell atoms

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KITP
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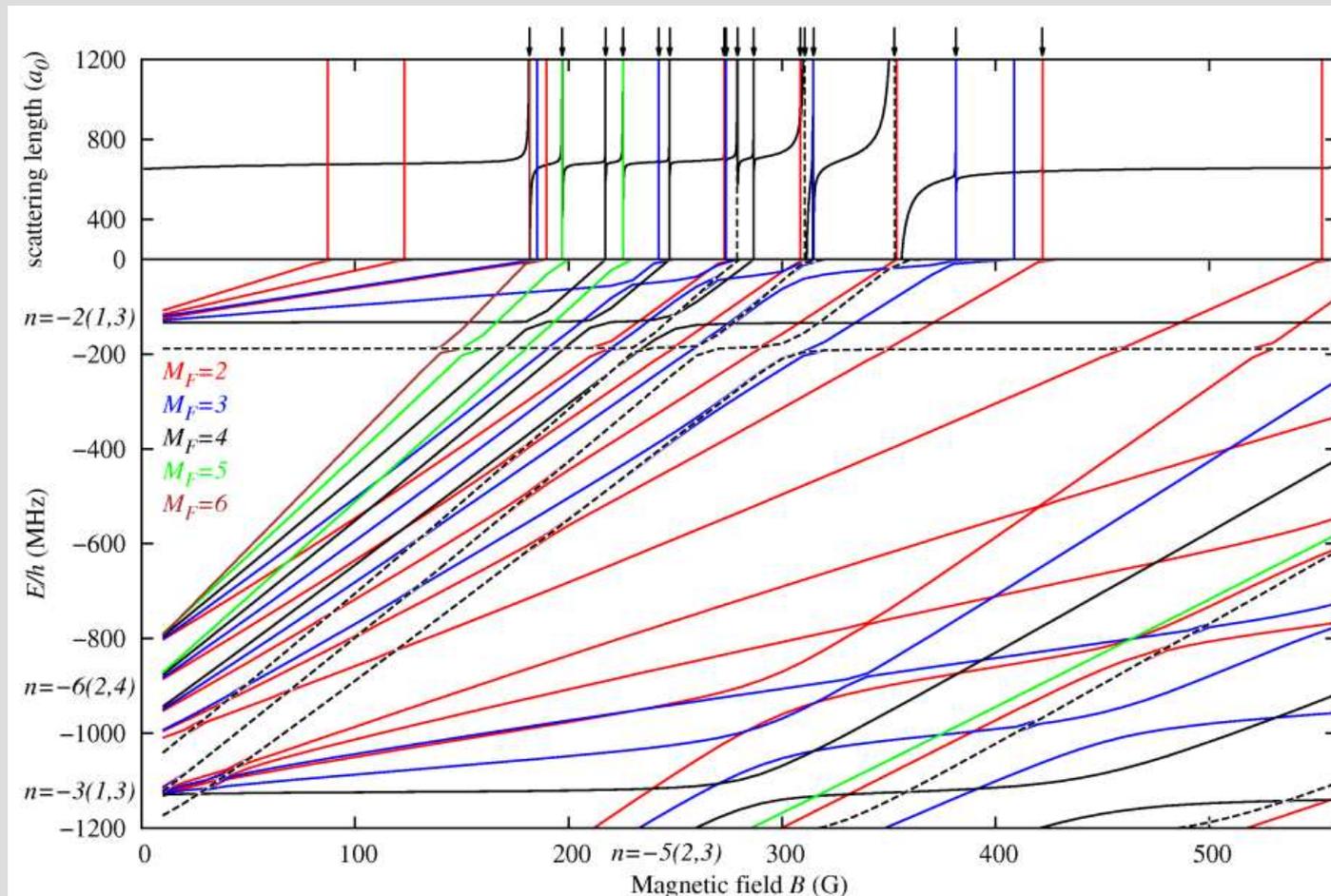
Magnetoassociation to form alkali dimers



- Tune directly from atomic state (separated atoms) to molecular state by sweeping the magnetic field slowly (adiabatically) over an avoided crossing (Feshbach resonance)
- Magnetoassociation makes molecules in a single state, so a good starting-point for STIRAP to reach absolute ground state
- Alkali-metal dimers all have singlet ground states: no electron spin
- We would like to extend magnetoassociation to molecules with electron spin as well as electric dipole
- Molecules formed from an alkali-metal atom (2S) and a closed-shell atom (1S , e.g. Sr, Yb) are a good option

Magnetoassociation to form alkali-metal dimers

- For alkali dimers, there is a complicated pattern of near-dissociation molecular levels below each atomic threshold, which can be tuned across threshold with magnetic fields
- A zero-energy Feshbach resonance occurs where each level crosses threshold. For example, for $^{87}\text{Rb}^{133}\text{Cs}$ below the lowest (aa) threshold:

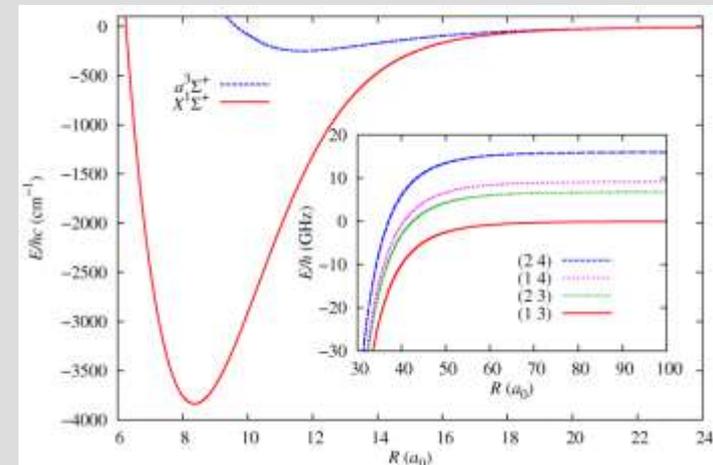


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- A zero-energy Feshbach resonance occurs where each level crosses threshold. For example, for $^{87}\text{Rb}^{133}\text{Cs}$ below the lowest (aa) threshold:
- Alkali-metal atoms all have non-zero nuclear spin i and $s=\frac{1}{2}$
- Atomic quantum numbers are $f=i\pm\frac{1}{2}$ (at low field) and m_f
- Alkali dimers ($^2S+^2S$) have 2 potential curves, singlet ($S=0$) and triplet ($S=1$)
- Collision Hamiltonian is

$$H = T + \xi_a i_a \cdot s_a + \xi_b i_b \cdot s_b + H_{\text{Zeeman}} + \sum_S |S\rangle V_S(R) \langle S| + V_{\text{dipolar}}(R)$$

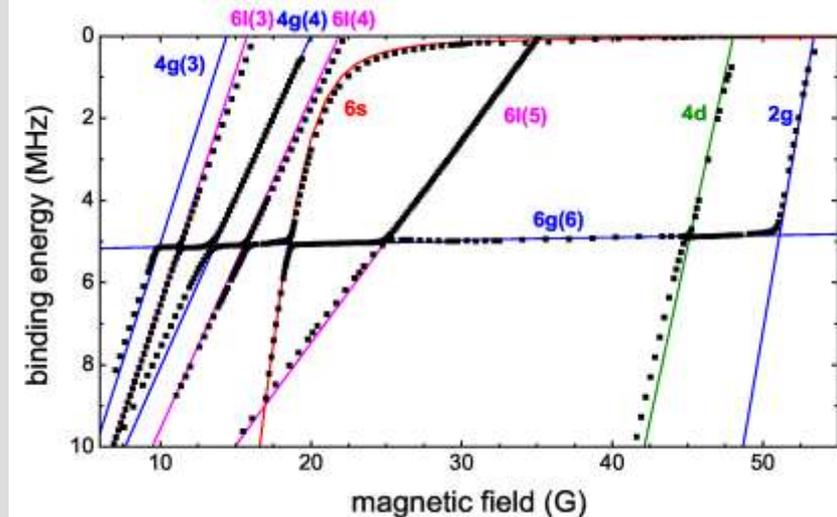
- Molecular states have *different* spin character to atomic states
- Hamiltonian couples molecular states to atomic states
=> Feshbach resonances



The need for theory

- Need potential curves that reproduced energy levels to understand level patterns and avoided crossings for full control
- For two 2S atoms there are 5 sources of angular momentum:
 - 2 electron spins
 - 2 nuclear spins ($I=7/2$ for ^{133}Cs)
 - Mechanical rotation (L or N)
- In a magnetic field only M_{tot} is conserved (not total angular momentum)
- Basis set $(s_a i_a f_a)(s_b i_b f_b) F M_F L M_L M_{\text{tot}}$ or fully decoupled: labels such as $6g(6)$ indicate $FL(M_F)$ [s, p, d... for $L=0,1,2...$]
- Homonuclear dimer is a special case: Far from avoided crossings, F, M_F and L are nearly conserved, and a small basis set is adequate
- Near avoided crossings, nothing but M_{tot} is conserved: over 200 spin basis functions (channels) sometimes needed.
- Hamiltonian couples everything:

$$H = T + \xi_a i_a \cdot s_a + \xi_b i_b \cdot s_b + H_{\text{Zeeman}} + \sum_S |S\rangle V_S(R) \langle S| + V_{\text{dipolar}}(R)$$



Use coupled-channel expansion for molecular wavefunction

$$\Psi_n = \sum_i \Phi_i(SIL)\psi_i(R)$$

where $\Phi_i(SIL)$ are basis functions for (all the) angular momenta.

Substitute in Schrödinger equation to produce coupled radial equations:

$$\frac{d^2\psi_{jn}}{dR^2} = \sum_k [W_{jk}(R) - E_n\delta_{jk}] \psi_{kn}(R)$$

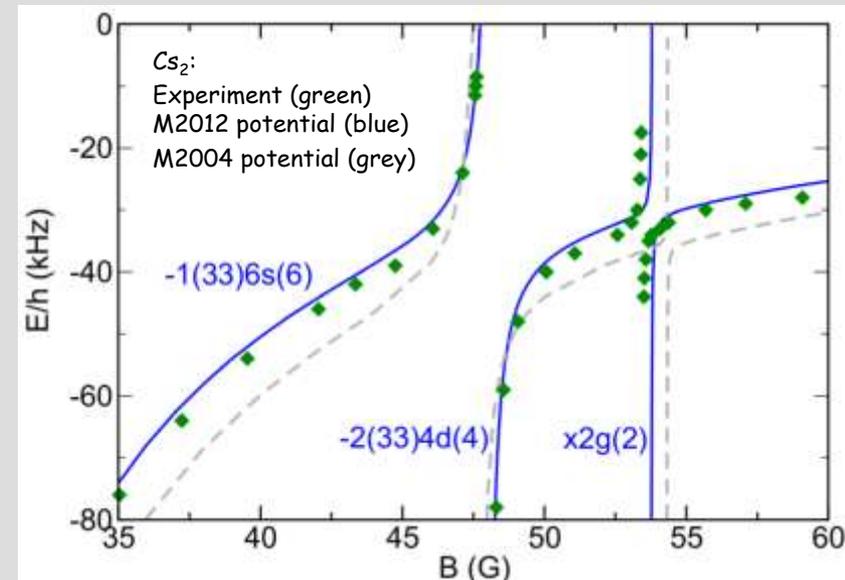
For scattering, propagate coupled equations from short range ($R \sim 5 a_0$) to long range (1000 to 10000 a_0) and match to Bessel functions to get S -matrix; then scattering length $a(k) = (ik)^{-1} (1-S_{00})/(1+S_{00})$

MOLSCAT program can converge on resonances [poles and zeroes in $a(B)$]

Bound-state calculations (BOUND program) also use coupled-channel propagation approach, *not* radial basis set

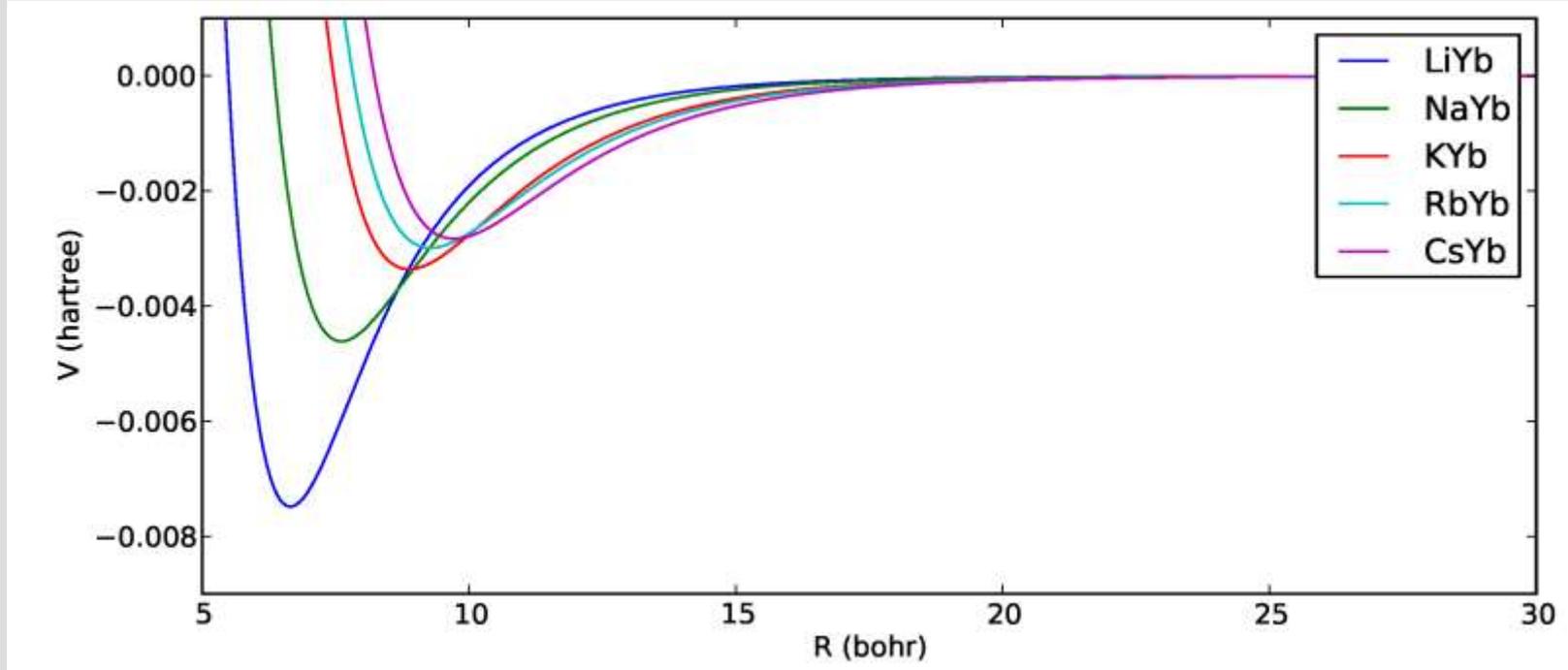
- Time *linear* in number of steps: no problem handling 200+ channels
- Can propagate quickly to very long (Airy-based log-derivative propagator)
- Can easily find bound states within 10 kHz of dissociation

BOUND and MOLSCAT implement many different collision systems (alkali-alkali, atom-molecule, molecule-molecule): can plug in new subroutines for new cases.



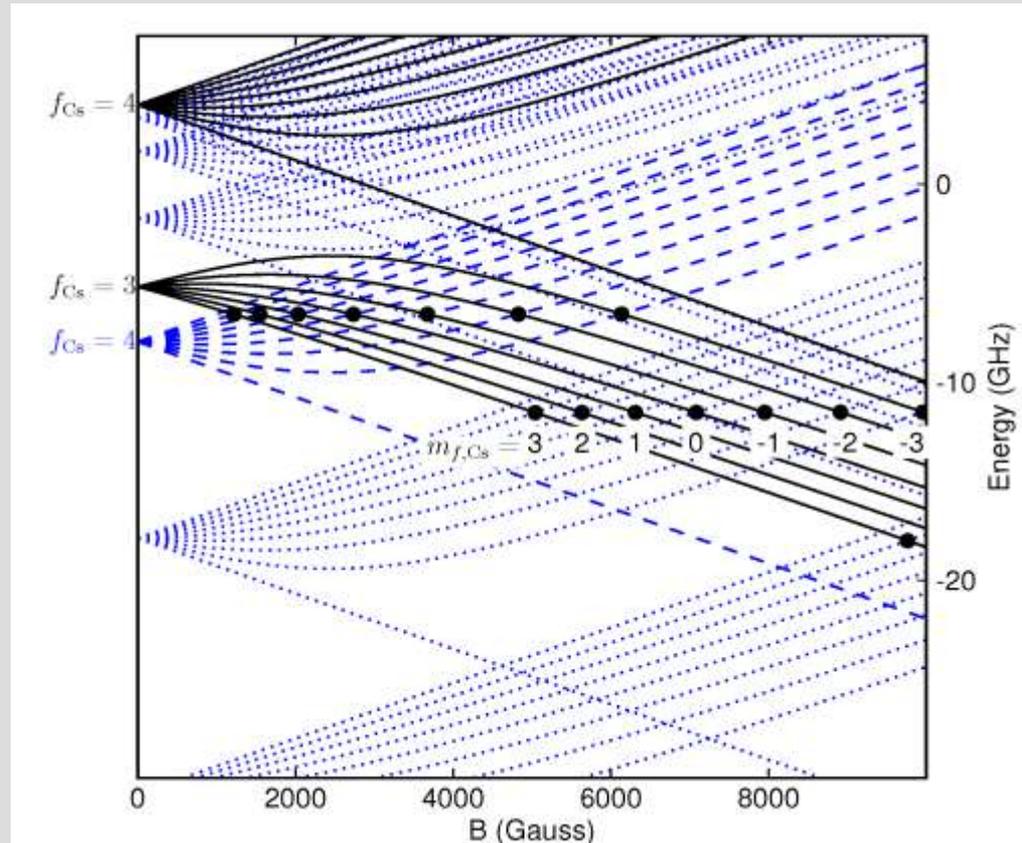
What is different for alkali (2S) + 1S atom systems?

- Only one molecular electronic state: $^2\Sigma$
- The molecular Hamiltonian
$$H = T + V(r) + \xi i.s + H_{\text{Zeeman}}$$
is diagonal in atomic quantum numbers
- Curves correlating with different atomic hyperfine / Zeeman states are essentially parallel to one another (shifted by atomic energy)



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- Curves correlating with different atomic hyperfine / Zeeman states are essentially parallel to one another (shifted by atomic energy)
- The molecular states lie parallel to the atomic thresholds (as a function of field) and have the same character
- There are crossings between molecular levels with $f=i+\frac{1}{2}$ and atomic thresholds with $f=i-\frac{1}{2}$ but no coupling
- \Rightarrow Feshbach resonances have zero width (i.e. do not exist)
- Fortunately, this is an oversimplification!

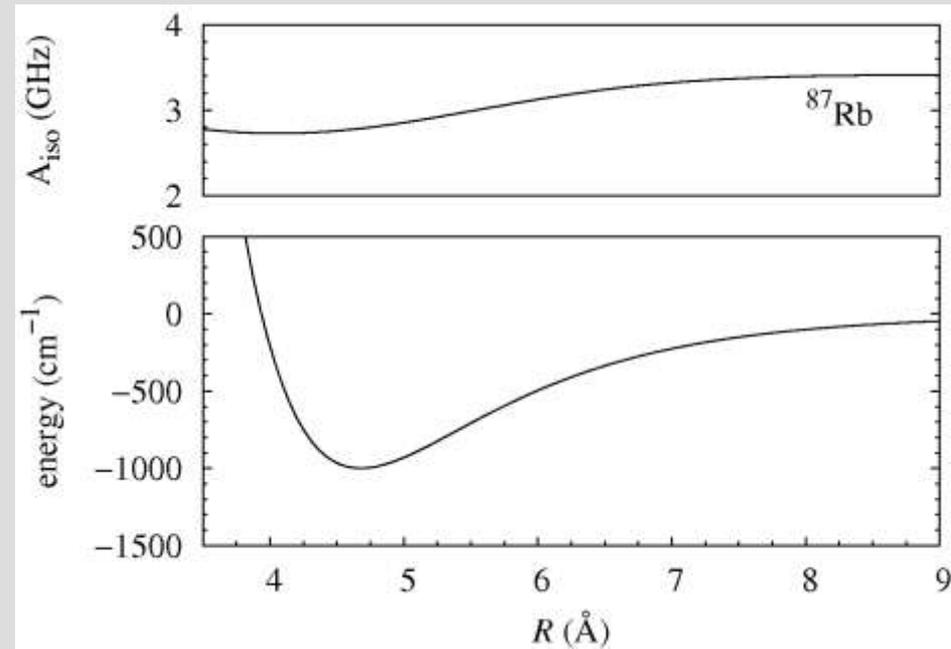


What makes magnetoassociation allowed?

- What is there in the collision Hamiltonian that can couple states with the same L and m_f but different f ? Usual Hamiltonian would be

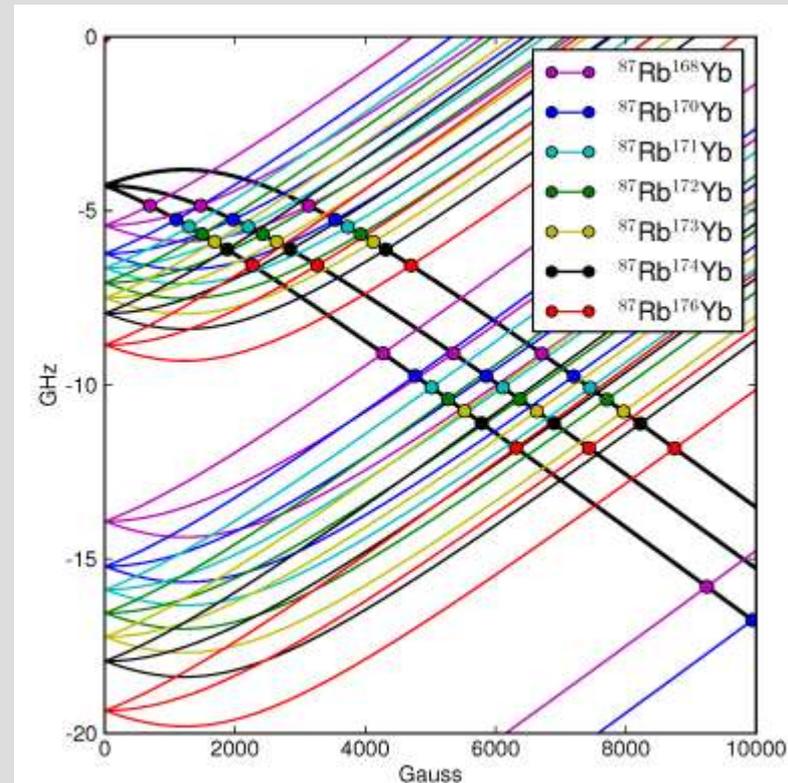
$$H = T + V(R) + \xi \mathbf{i} \cdot \mathbf{s} + B_z (g_i i_z + g_s s_z)$$

- The atomic hyperfine interaction does *not* provide such a coupling: f is not a good quantum number at finite field, but the atomic and molecular states are nondegenerate eigenfunctions of $\xi \mathbf{i} \cdot \mathbf{s} + B_z (g_i i_z + g_s s_z)$ so are orthogonal \Rightarrow no coupling from an R -independent ξ
- But the atomic hyperfine coupling is actually *modified significantly at short range* by the presence of the 2nd atom
- This provides a coupling that *does* mix the atomic and molecular states and can cause Feshbach resonances



Scattering lengths and masses

- As for the alkali-metal atoms, no *ab initio* potential is good enough to predict the absolute values of scattering lengths / binding energies: experimental measurements are essential.
- *But* once a binding energy is known for one isotopic combination, the *ab initio* potentials *are* good enough to predict mass-scaling.
- For heavier alkalis, binding energies (and thus crossing positions) depend substantially on isotope. E.g. for $^{87}\text{RbYb}$:
- Axel Görlitz's group (Düsseldorf) has now measured binding energies for a several isotopologues of $^{87}\text{Rb}^{\text{xxx}}\text{Yb}$.
- These allow fitting to produce potential curves to estimate resonance positions for any $^{85}\text{RbYb}$ or $^{87}\text{RbYb}$ species.
- But what are the widths?



How wide are the Feshbach resonances?

- Initial work on RbSr (using coupled-channel calculations) [PRL 105, 153201 (2010)] found resonance widths from 0.3 μG to 100 mG at fields between 30 G and 5000 G
- The numbers are right, but they don't provide much understanding!
- We have now developed a quantitative model based on Fermi Golden Rule that gives both insight and quantitative predictions of widths
- The Golden Rule gives a resonance width Γ (in energy) as

$$\Gamma = 2\pi \left| \int \Psi_{\text{bound}}^* H' \Psi_{\text{free}} d\tau \right|^2$$

- This allows the magnetic field width Δ to be expressed as

$$\Delta = \pi [I_{m_f}(B)]^2 (I_{nk}^2/k) / (a_{\text{bg}} \delta\mu_{\text{res}})$$

- $I_{m_f}(B)$ is a purely atomic matrix element of $i.s$ between the two (field-dressed) states with a given f, m_f
- I_{nk} is a purely radial matrix element of $\Delta\xi(R)$ between the bound state and the continuum function at wavevector k (and I_{nk}^2/k is independent of k at low energy)
- a_{bg} is the background scattering length (for 1-channel scattering)
- $\delta\mu_{\text{res}}$ is the magnetic moment difference between the bound and free states (relative slope of the crossing states)

Atomic spin part gives strong field-dependence

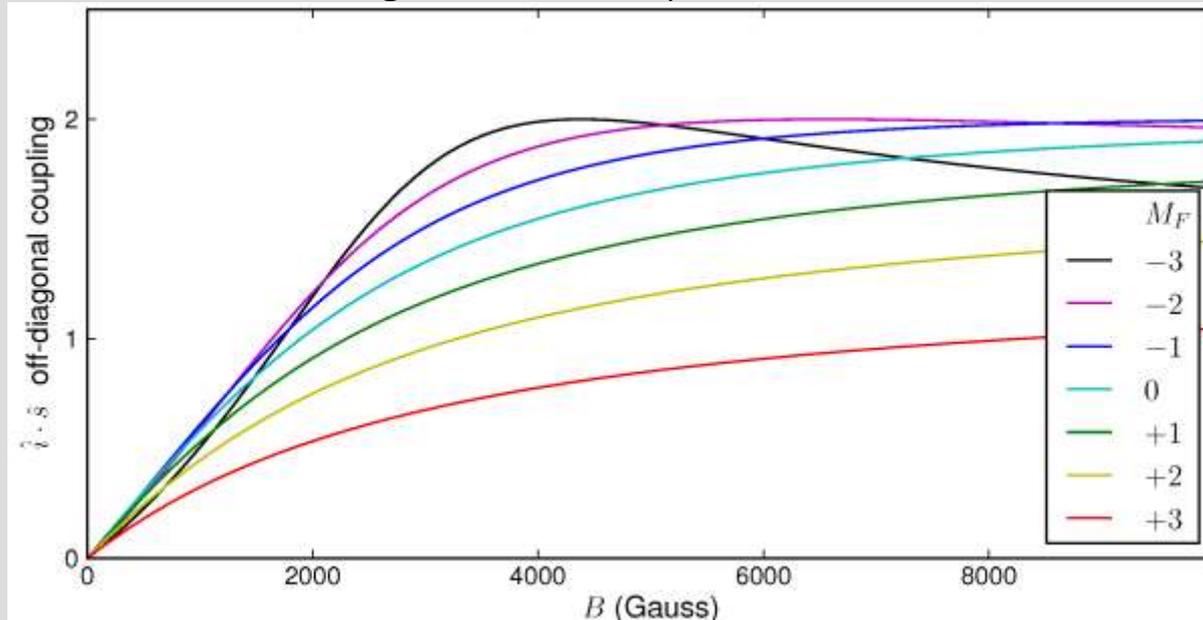
$$\Delta = \pi [I_{mf}(B)]^2 (I_{nk}^2/k) / (a_{bg} \delta\mu_{res})$$

$$I_{mf}(B) = \langle \alpha_{1,m_f} | i.s | \alpha_{2,m_f} \rangle \quad (\text{between purely atomic field-dressed states})$$

- At limitingly high B , m_s and m_i are good quantum numbers and this reduces to $[I_{mf}(B)]^2 = \frac{1}{4}[i(i+1)-m_f^2+\frac{1}{4}]$ (from raising and lowering operators i_{\pm} etc.)
- *But* the zero-field atomic states are eigenfunctions of $i.s$
 $\Rightarrow I_{m_f}(B)$ is zero at zero field and increases linearly with field
 \Rightarrow resonances that occur at low field have widths proportional to B^2 .

Consequences for experiment:

- Low-field resonances are probably not a good bet:
Need to design experiments to work at high field
- High-spin alkali metals have intrinsic advantages over low-spin ones

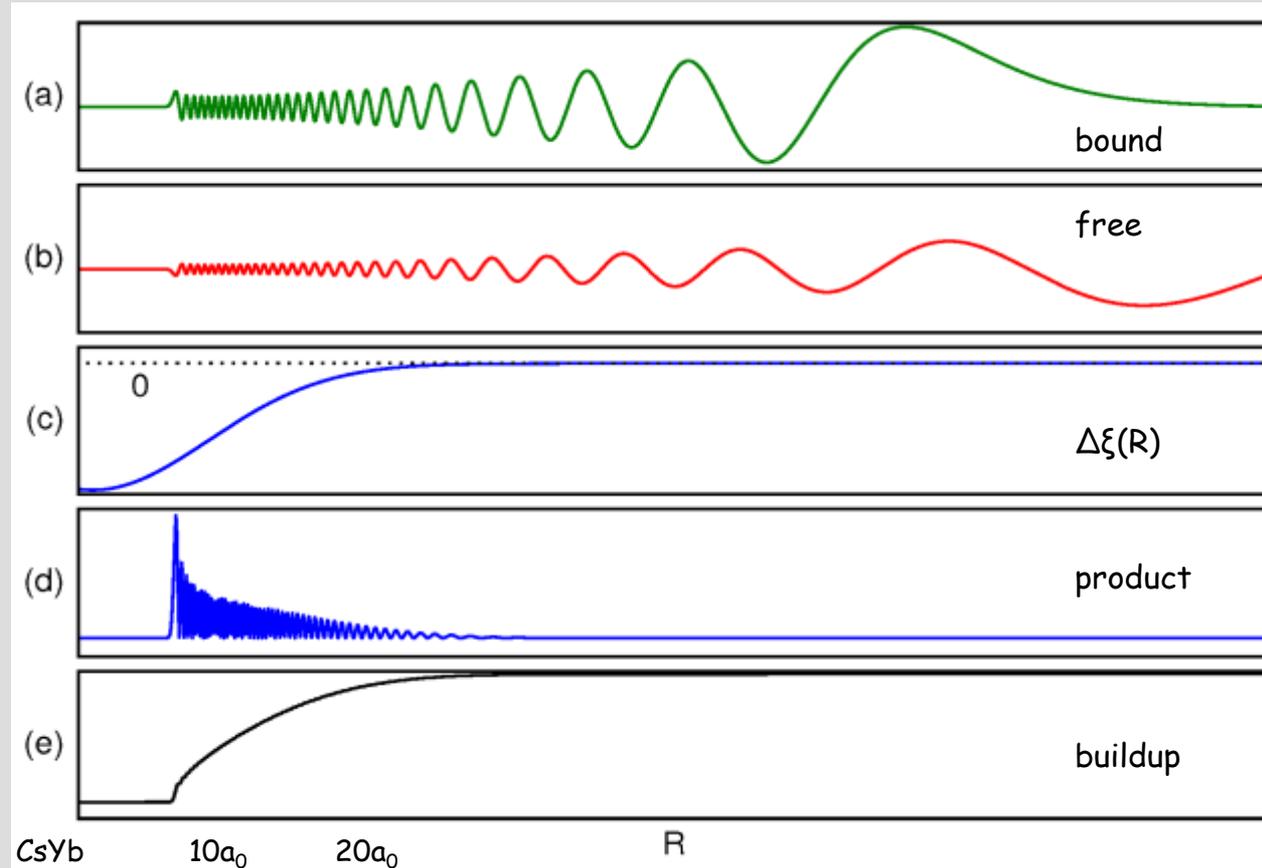


Radial integral is dominated by short range

$$\Delta = \pi [\mathcal{I}_{mf}(B)]^2 (\mathcal{I}_{nk}^2/k) / (a_{bg} \delta\mu_{res})$$

$$\mathcal{I}_{nk} = \int \psi_{bound}^* \Delta\xi(R) \psi_{free} dR \quad (\text{between 1-d radial functions on same potential})$$

- Atomic and molecular states are orthogonal so R-independent term in $\xi(R)$ does not couple them; only $\Delta\xi(R)$ contributes and short range dominates
- Molecular state bound by < 10 GHz so stays almost in-phase with continuum

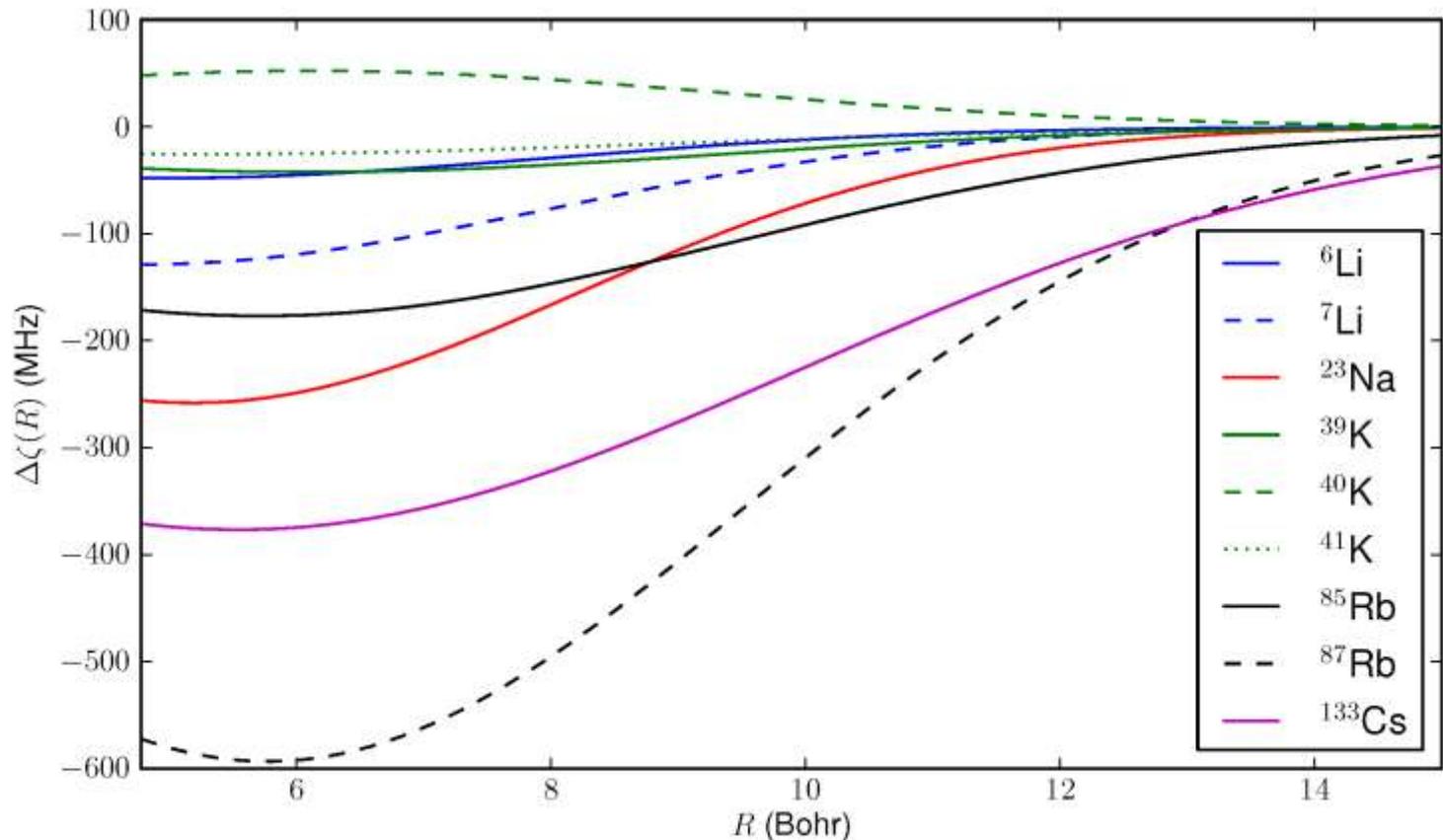


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- Atomic and molecular states are orthogonal so R-independent term in $\xi(R)$ does not couple them; only $\Delta\xi(R)$ contributes and short range dominates
- Molecular state bound by < 10 GHz so stays almost in-phase with continuum
- $\Delta\xi(R)$ is roughly proportional to ξ so heavy alkali metals give greater widths



Other factors

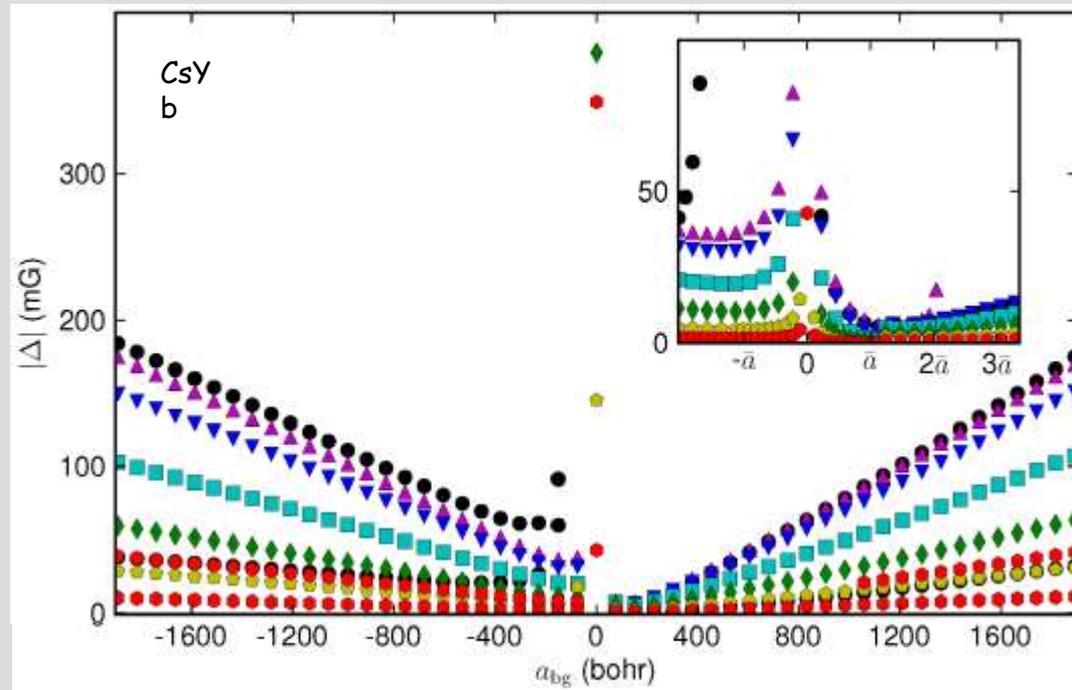
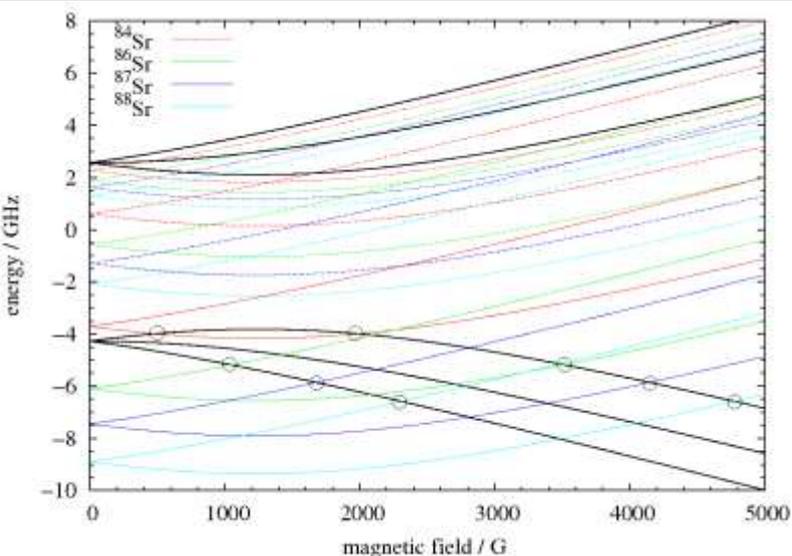
$$\Delta \text{ proportional to } \left| \int \psi_{\text{bound}}^* \Delta \xi(R) \psi_{\text{free}} dR \right|^2 / a_{\text{bg}}$$

Large widths for very small a_{bg} are not really useful ($a_{\text{bg}}\Delta$ more relevant than Δ)
 But continuum normalisation at short range is proportional to $[1+(1-a_{\text{bg}}/a(\text{bar}))^2]^{1/2}$

=> Width is proportional to $|a_{\text{bg}}|$ when $|a_{\text{bg}}| \gg a(\text{bar})$

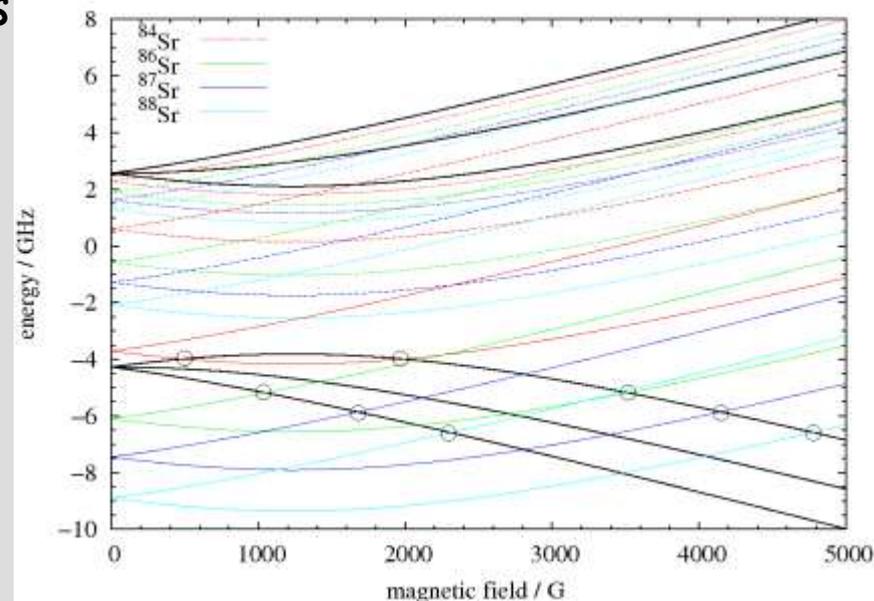
Systems with large scattering length give the broadest resonances
 (but beware phase separation, as in $^{174}\text{Yb} + ^{87}\text{Rb}$ (Baumer et al.))

Molecular states that "kiss"
 the threshold (small $\delta\mu_{\text{res}}$)
 also give broad resonances



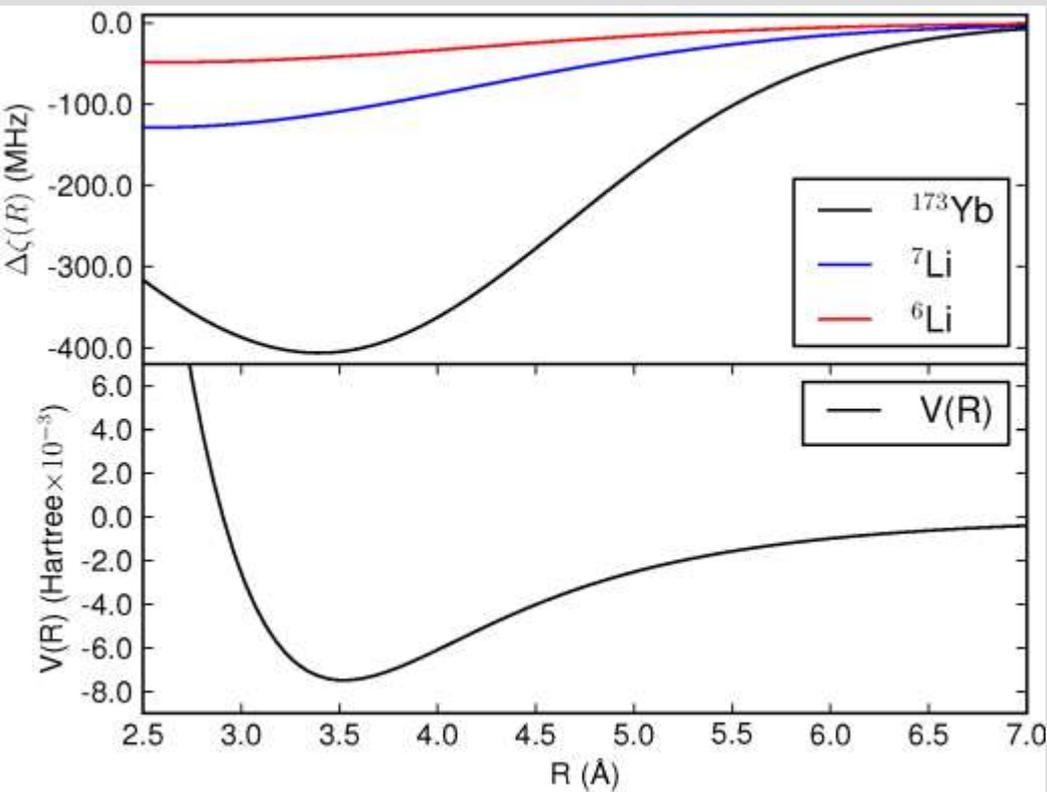
How wide are the Feshbach resonances in RbYb?

- $^{85}\text{YbRb}$ has some resonances below 1000 G but they are very narrow
 - $^{85}\text{Rb}^{174}\text{Yb}$ 1.5 μG near 100 G
 - $^{85}\text{Rb}^{176}\text{Yb}$ 0.9 mG near 900 G
- This illustrates the general B^2 dependence of widths at low field!
- $^{87}\text{YbRb}$ has much wider resonances but at higher field
 - $^{87}\text{Rb}^{168}\text{Yb}$ 0.6 mG near 800 G (low abundance)
 - $^{87}\text{Rb}^{170}\text{Yb}$ 6 mG near 2100 G
 - $^{87}\text{Rb}^{174}\text{Yb}$ 5 mG near 3000 G
- *None* of the $^{87}\text{RbYb}$ isotopologues is "lucky" enough to give double crossings that would result in enhanced widths



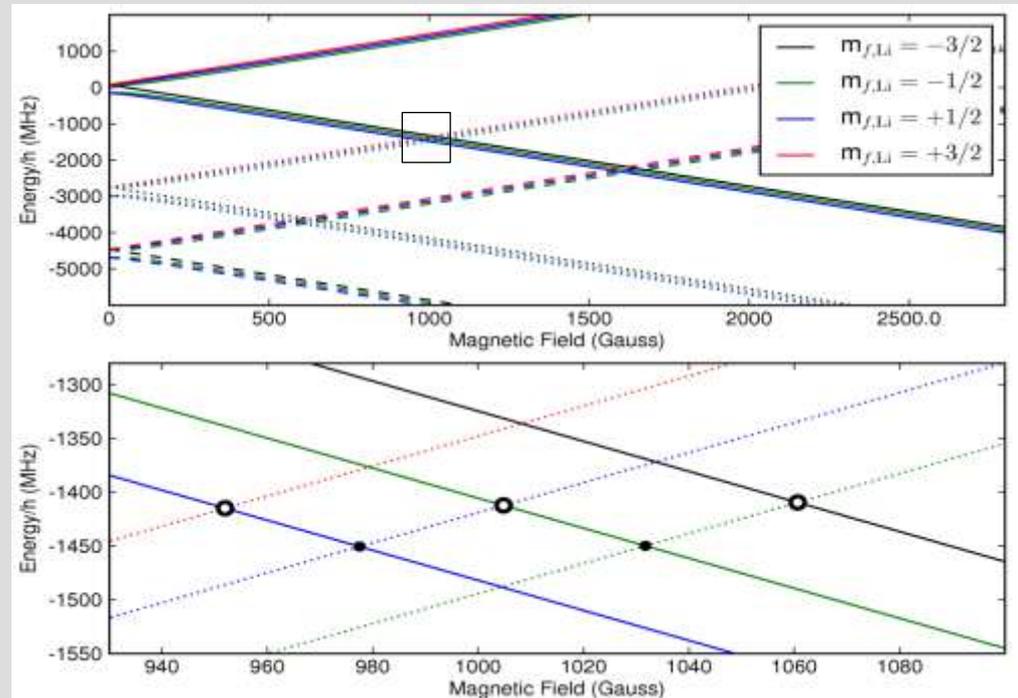
What about LiYb? (Gupta, Washington; Takahashi, Kyoto)

- Very little mass-scaling with Yb isotope
- Scattering length measured as $|a| = 8(2) \text{ \AA}$
- Widths are tiny for bosonic Yb (e.g. 2 \mu G for ${}^6\text{Li}^{174}\text{Yb}$ near 1000 G)
- But there is another possibility: bond formation transfers spin density from Li to Yb, so Li^{171}Yb and Li^{173}Yb have hyperfine coupling from i_{Yb}
- $\Delta\xi(R)$ is considerably larger for Yb \Rightarrow wider resonances



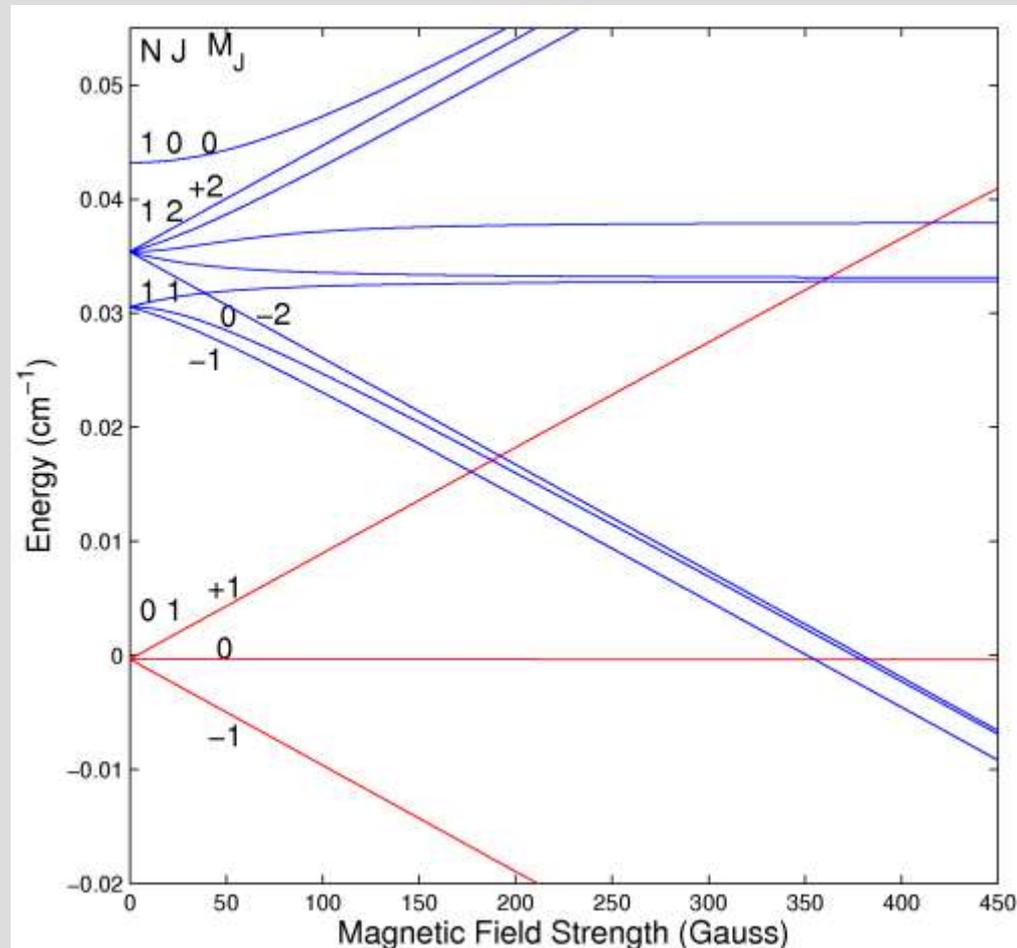
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- Yb resonances have different selection rules: $\Delta m_s = -\Delta m_{\text{Yb}} = \pm\frac{1}{2}$
- These are *decaying* resonances, but still pole-like
- Widths are around 0.2 mG
- This mechanism *will* give additional resonances for other alkalis, but not dramatically wider ones.



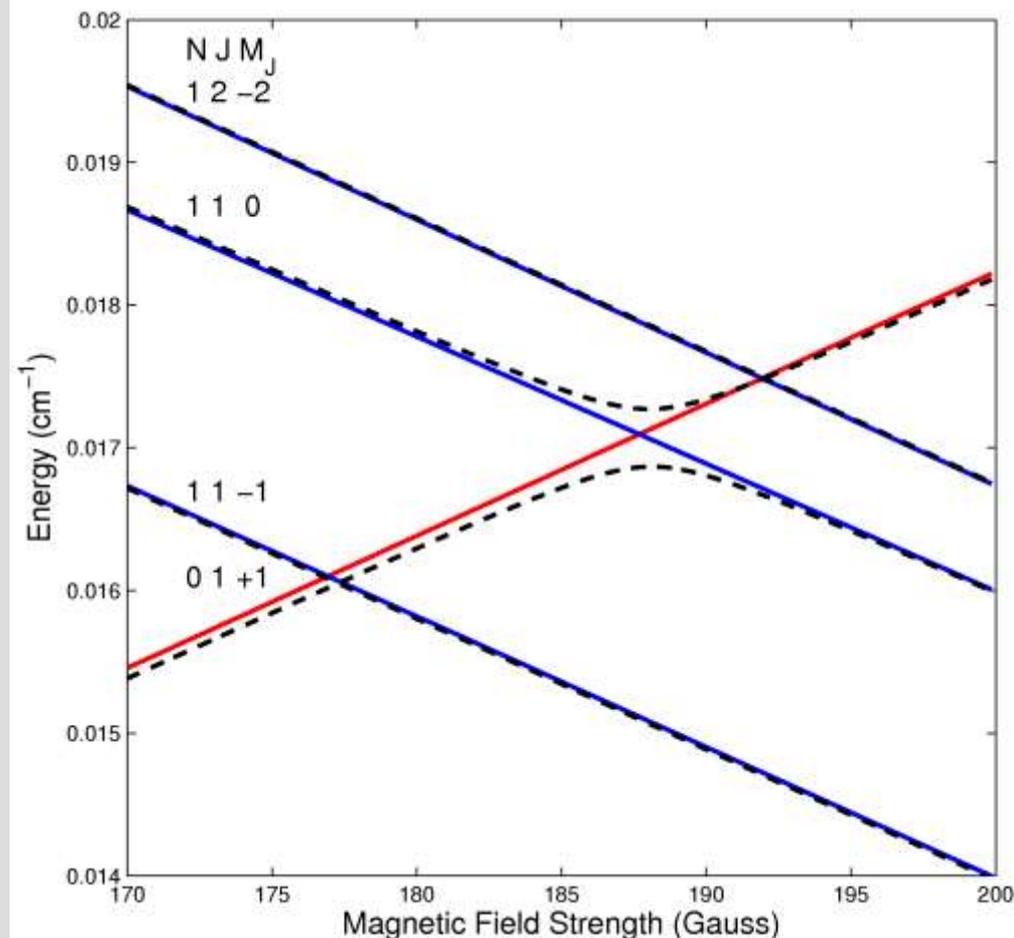
Conical intersections with ultracold molecules

- For a molecule with both an electron spin and an electric dipole moment, e.g. KRb ($^3\Sigma$) or RbSr ($^2\Sigma$)
- Two levels of different parity (different rotational quantum number) may cross as a function of magnetic field
- For polar molecules, an electric field can mix these two states



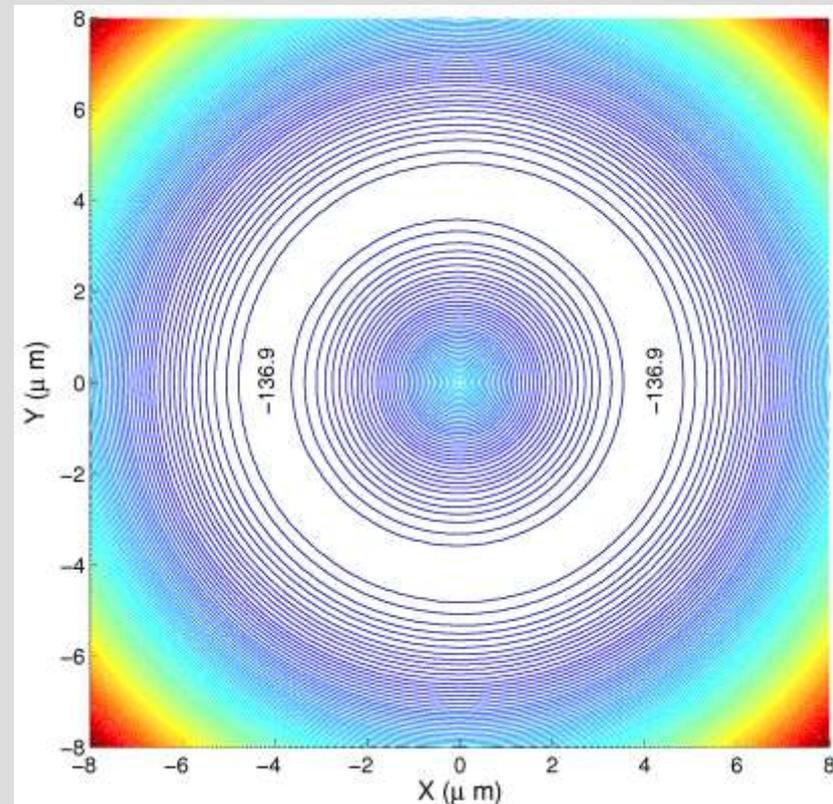
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- For polar molecules, an electric field can mix these two states
- Could create a *conical intersection* between eigenstates at the point where the Zeeman states are degenerate *and* the electric field passes through zero
- Adding an optical potential produces a potential minimum that is nearly isotropic around a ring
- For bosonic $^{41}\text{K}^{87}\text{Rb}$, fields here are:
 - $B_z = 187 \text{ G}$
 - $\text{dB}_z/\text{dX} = 5 \text{ G/cm}$
 - $\text{dF}/\text{dY} = 6.7 \text{ kV/cm}^2$
 - optical trap depth $7 \text{ } \mu\text{K}$ at $30 \text{ } \mu\text{m}$.

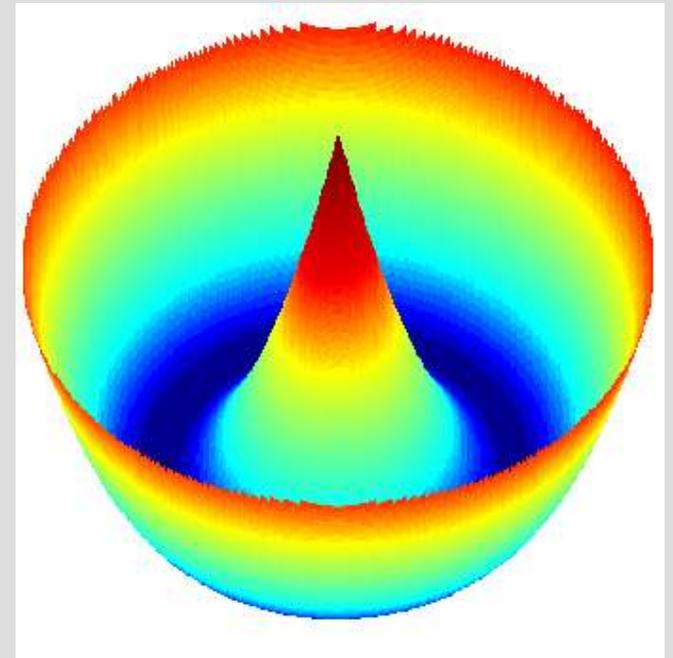


Vortices with half-integer quantisation

- BEC is stable all around the ring if $a_{11} > 0$, $a_{22} > 0$ and $2a_{12} > -(a_{11}+a_{22})$.
- A conical intersection produces a *Berry phase*: along a path that encircles the intersection once, the internal molecular wavefunction (molecular rotation + spin) adiabatically changes sign.
The resulting *twisted boundary condition* $\Phi(\varphi+2\pi) = -\Phi(\varphi)$ produces half-integer quantisation for a particle on a ring.
- In the Gross-Pitaevskii equation, persistent flow with half-integer angular momentum occurs if the chemical potential is large enough to overcome any residual anisotropy around the ring.
- The path around the conical intersection is originally slanted (because the crossing states have different magnetic moments) but this can be compensated with a small offset of the optical trap.

PRL 103, 083201 (2009)

- A variant based on microwave dressing could be applied to ^{87}Rb : PRA 84, 051402(R) (2011).
- Cute... But what is it good for?



Conclusions

- Atom pairing methods (magnetoassociation followed by STIRAP) can already produce ground-state alkali dimers below $1\ \mu\text{K}$ [so far, KRb (JILA), Cs_2 (Innsbruck) + others by incoherent approaches].
- Magnetoassociation may be possible for alkali + Yb, alkali + Sr, etc.
- Widest resonances occur for heavy alkali metals at high fields
- Careful choice of Yb or Sr isotope is very important, and requires measurement of binding energy or scattering length for one isotopic combination
- Conical intersections may produce intriguing new physical effects
- Other topics we're working on:
 - Sympathetic cooling with ultracold H atoms (Maykel Leonardo González-Martínez)
 - MQDT for molecular collisions (James Croft)
 - Molecule formation in $^{87}\text{RbCs}$ (Ruth LeSueur with Innsbruck etc.)
 - Feshbach resonances in $^{85}\text{RbCs}$ and $^{85}\text{Rb}_2$ (Caroline Blackley with Simon Cornish)
 - Cs-Cs potentials for Efimov physics (with Rudi Grimm & Paul Julienne)
 - Li-Li potentials for Fermi gases at unitarity (with Selim Jochim & Paul Julienne)

Thanks to...

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