

Weakly bound states and controlled collisions of ultracold molecules

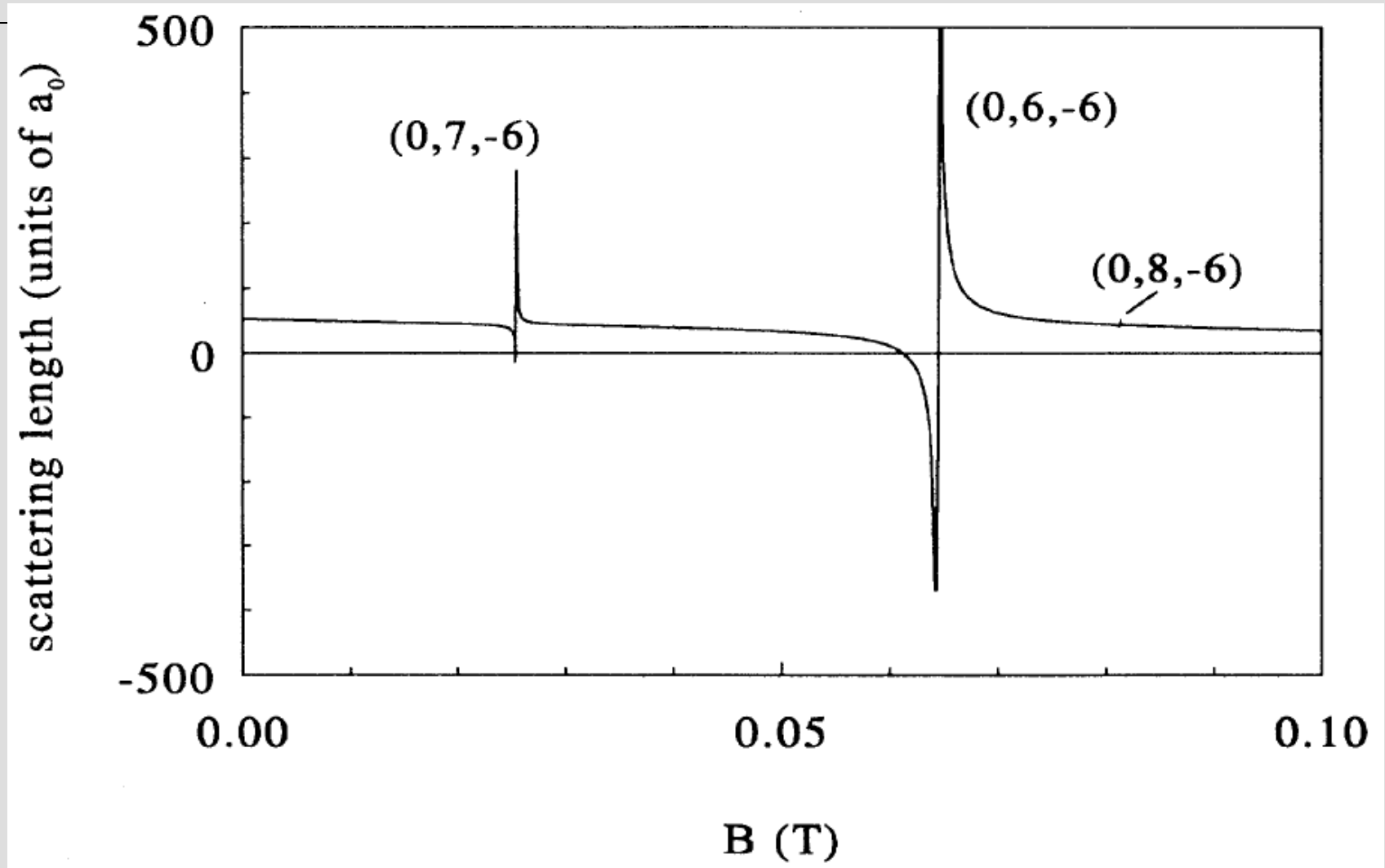
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Weakly Bound States workshop
Seattle, March 2010

Ultracold atoms and molecules

- For atoms and molecules, *ultracold* usually means below 1 mK (and ideally below 1 μ K)
- De Broglie wavelengths are large compared to molecular size
- Collisions mostly s-wave (incoming $L=0$)
- Collisions dominated by long-range forces and resonance phenomena
- Interactions can be *controlled* with applied fields (magnetic, electric, photon)
- Most applications depend on taking advantage of full quantum control

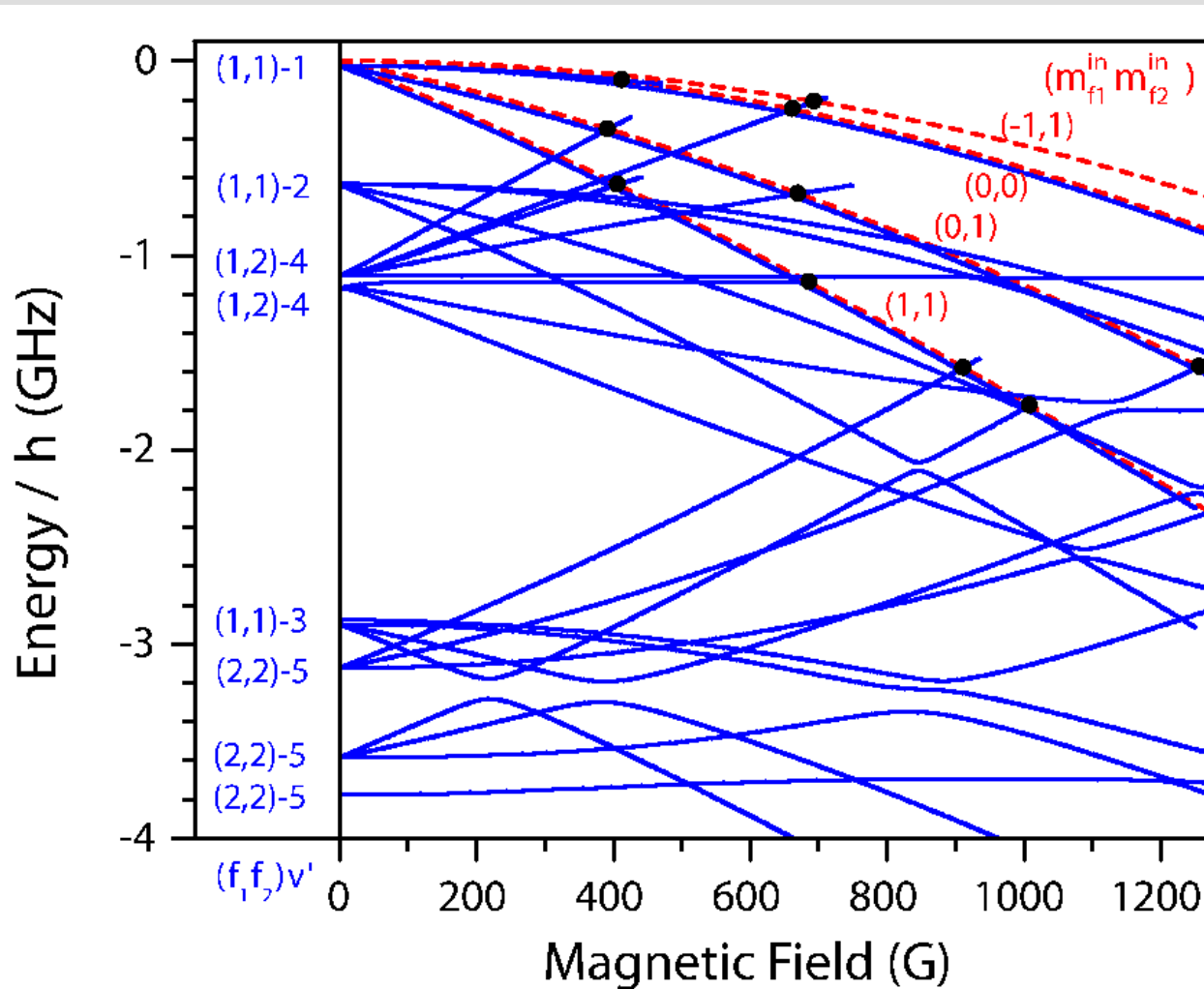
Control of collisions is through scattering length



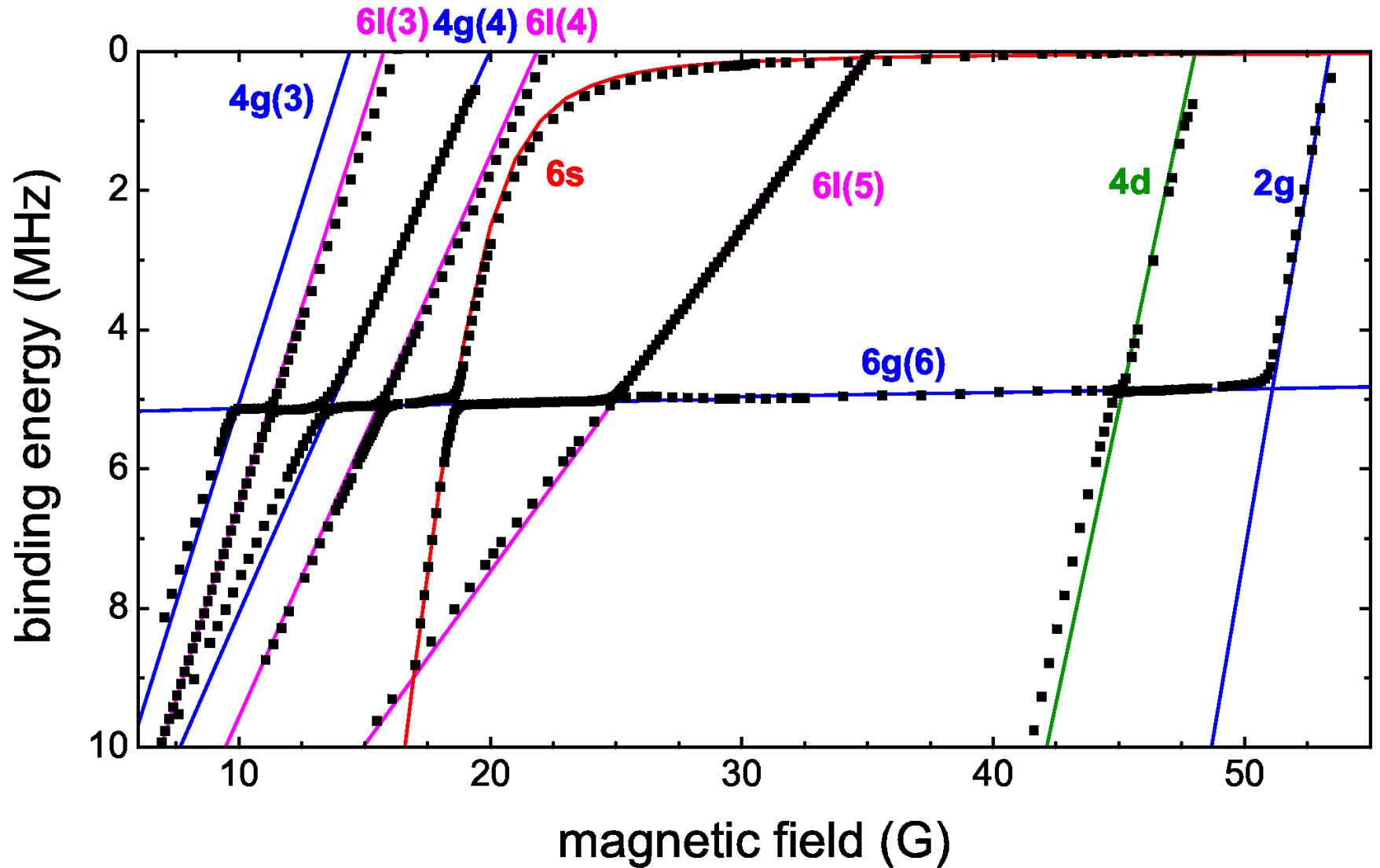
For atomic collisions, the scattering length a passes through a pole at resonance, so any desired value can be "dialed up"

Resonances occur where bound states cross threshold

Atomic dimers have many bound states near threshold.
Bound states (blue) and thresholds (red) have different Zeeman effects:
zero-energy Feshbach resonances occur where they cross

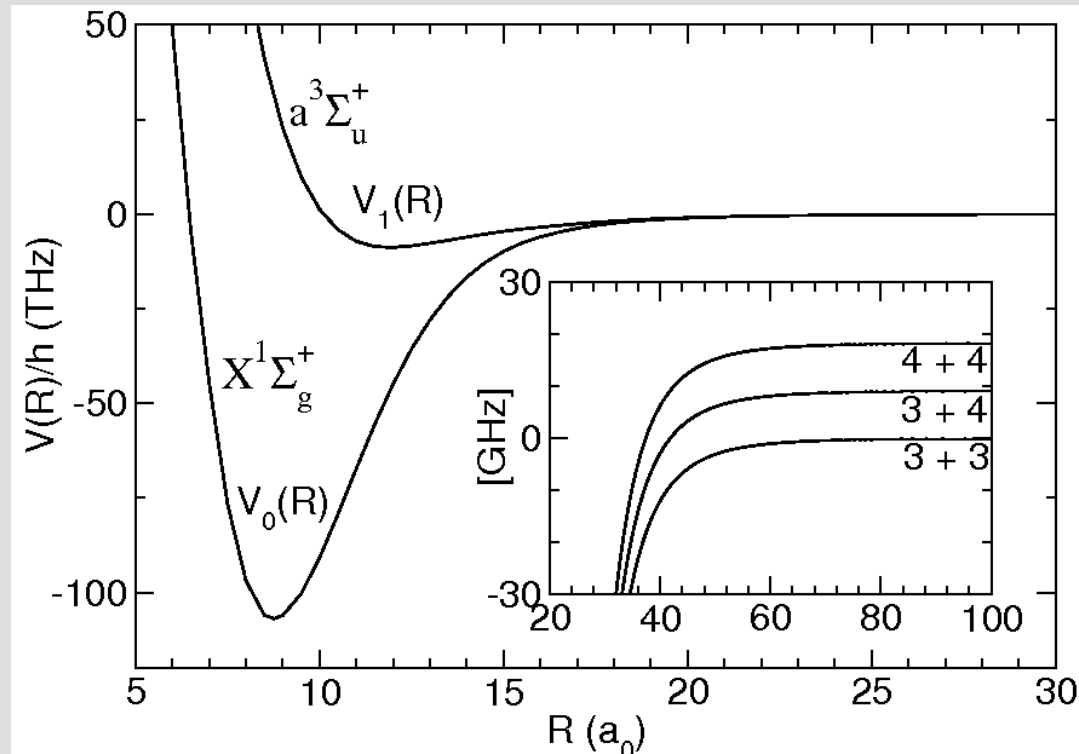


Overview of Cs_2 levels in top 10 MHz (10^{-7} of well depth) as function of magnetic field



Prototype problem: Cs_2

- 2-body problem involving highly structured particles: for Cs_2 , 2 electron spins, 2 nuclear spins, magnetic fields. Molecules are (much) more highly structured than atoms
- Potentials are local and real/Hermitian (no optical potentials) but may be many-dimensional, e.g. for molecule-molecule interactions
- Binding energy (well depth) is typically 100 THz or more
- Wavefunction oscillates very rapidly in inner region: can be hundreds of bound states per channel
- We are interested in states bound by between 1 kHz and 100 THz: 10 orders of magnitude [30 kHz = 1 μK]



How do we calculate the bound states?

- Not a 1-D problem: there are usually many internal degrees of freedom:
 - Electron spins (on both partners) s_A, s_B
 - Nuclear spins i_A, i_B (on both partners, several in a typical molecule)
 - Molecular rotation n_A, n_B
 - End-over-end rotation L
- E.g. for Cs dimer basis set could be $|s_A m_{sA}\rangle |i_A m_{iA}\rangle |s_B m_{sB}\rangle |i_B m_{iB}\rangle |LM_L\rangle$
Total angular momentum is not conserved in an applied electric or magnetic field
- Schrödinger equation can typically be written as a large coupled-channel problem
- A similar approach is applicable whenever there is a basis set for all coordinates except 1, e.g. 3-body system in hyperspherical coordinates

Schrödinger equation can typically be written as a large coupled-channel problem

$$\frac{-\hbar^2}{2\mu} \frac{d^2 \psi_{in}}{dR^2} = \sum_j \left[V_{ij}(R) - E \delta_{ij} \right] \psi_{jn}(R)$$

- Even for Cs dimer, we need over 200 channels in regions where states of different L interact with one another
- For atom-molecule problems, we may need tens of thousands of channels for convergence (e.g. >20,000 for Rb+OH)
- Molecule-molecule problems can be even worse

Possible approaches

- For few-channel problems, a radial basis set can be used:

$$\psi_{in} = \sum_m c_{im}^n \psi_m(R)$$

- For Cs_2 , with careful tailoring of the grid, good results can be obtained with a discrete variable representation (DVR) for $\psi_m(R)$, with around $N_R = 500$ radial basis functions per channel
- But note that for N_R radial functions and N_c channels, the time taken for a full diagonalization is proportional to $N_R^3 N_c^3$. This can be reduced a little when only some eigenfunctions are needed, but not enormously
- A much better approach is to use propagation methods:
 - Propagate the wavefunction from short range (R_{\min}) to a matching point R_{mid}
 - Propagate the wavefunction from long range (R_{\max}) to R_{mid}

History

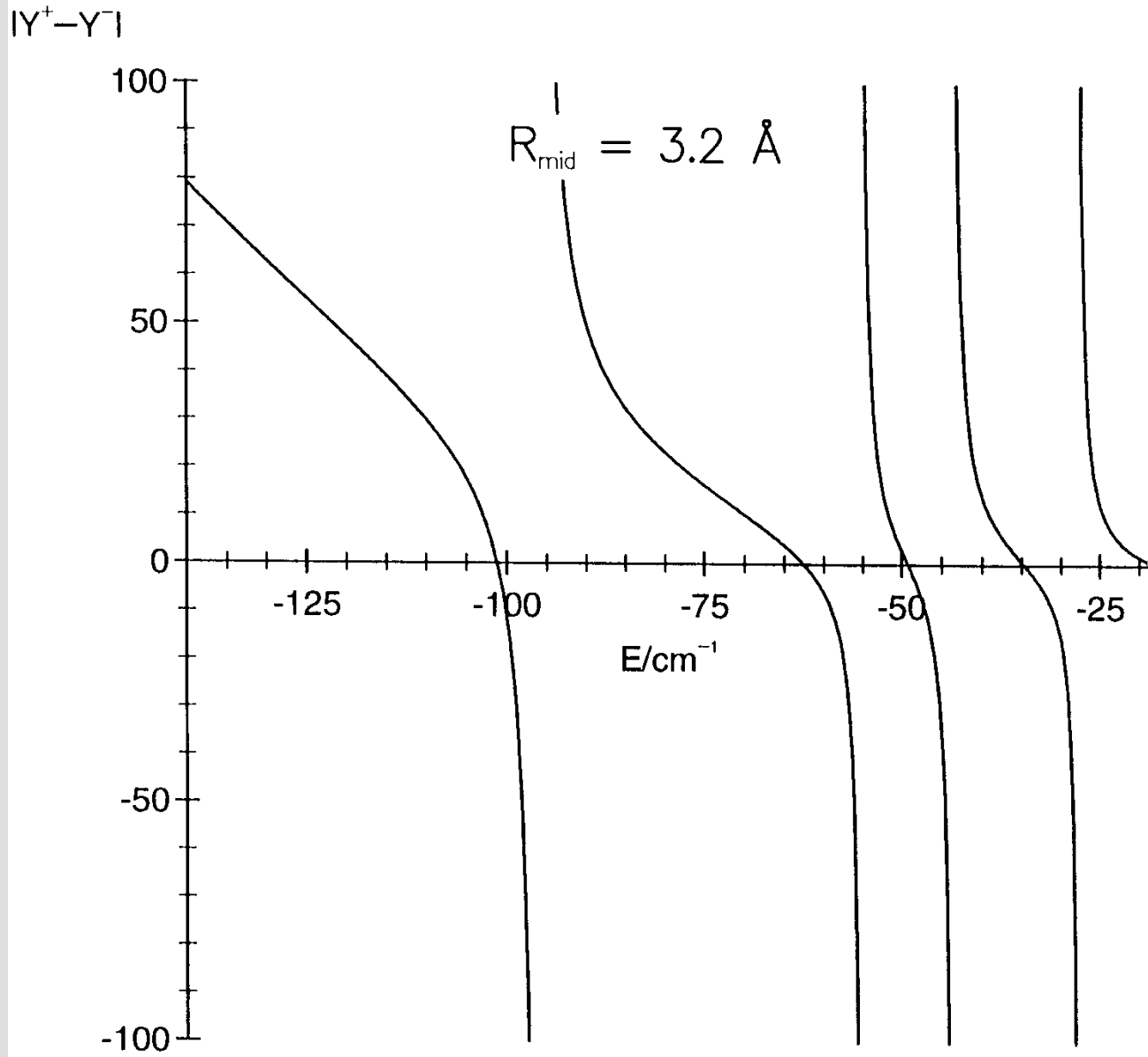
- 1-D version of this is Numerov-Cooley method (1961): wavefunction can always be renormalized to match at R_{mid} , but continuity achieved only if derivatives match too: search for match as function of energy.
- For coupled-channel problem, need to propagate wavefunction *matrix* $\Psi(R)$ [not vector $\psi(R)$] because there are N linearly independent solutions
- Original version by Roy Gordon (1969):
 - Propagate wavefunction matrix and its derivative
 - Search for zeroes of determinant of $2N \times 2N$ matching matrix (as function of energy)
 - Stability problem with closed channels (need frequent stabilizing transforms)

Log-derivative propagators are much stabler

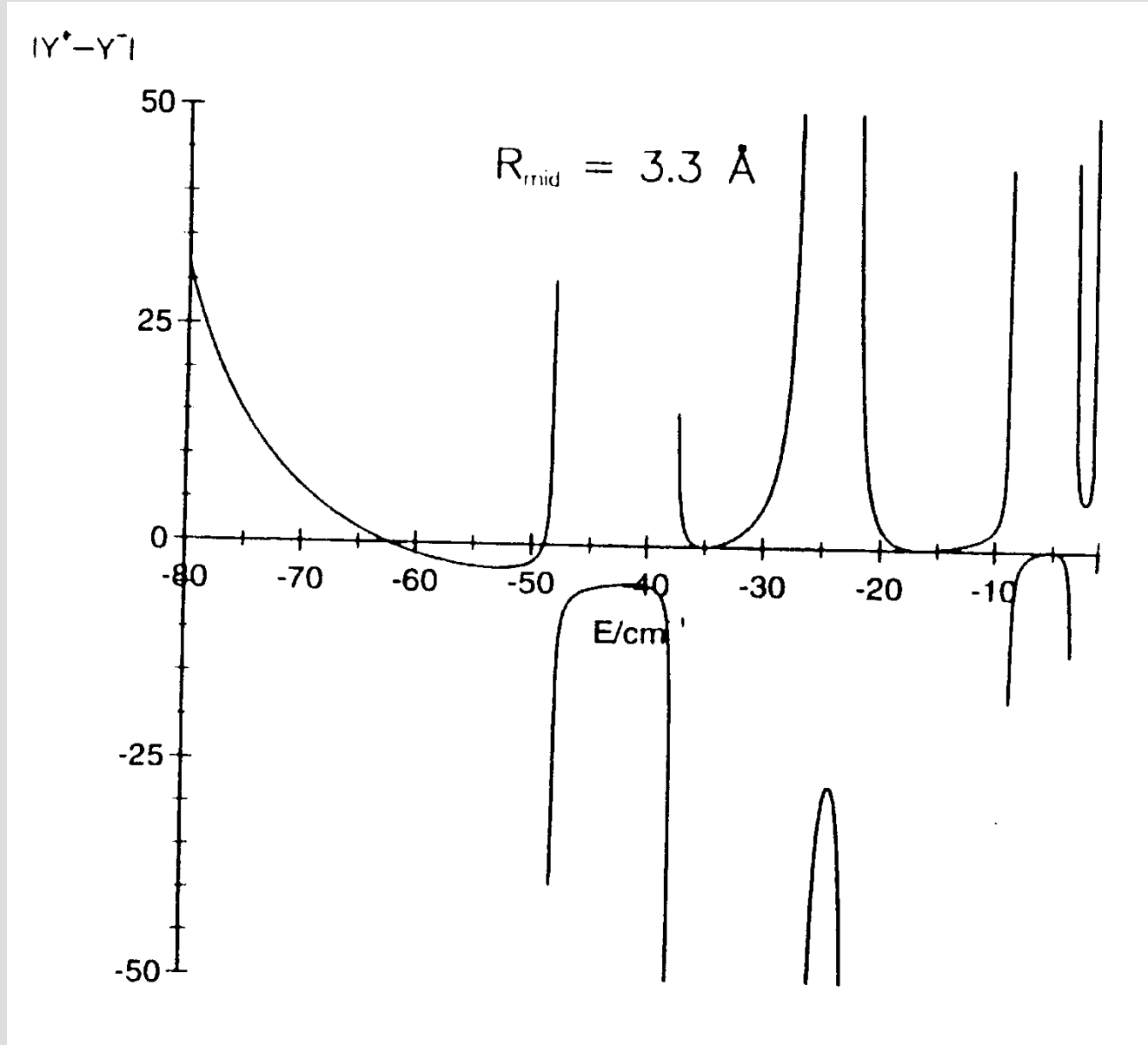
- Much stabler to propagate log-derivative matrix $Y(R) = \Psi^{-1} d\Psi/dR$ instead of $\Psi(R)$ itself
- Criterion for continuity at R_{mid} is that there must exist a wavefunction vector $\psi(R)$ such that
$$\psi(R) = \psi_{\text{in}}(R) = \psi_{\text{out}}(R)$$
and
$$d\psi_{\text{in}}(R)/dR = d\psi_{\text{out}}(R)/dR \quad \text{at } R = R_{\text{mid}}$$

i.e. $Y_{\text{in}}(R_{\text{mid}}) \psi(R_{\text{mid}}) = Y_{\text{out}}(R_{\text{mid}}) \psi(R_{\text{mid}})$
i.e. $[Y_{\text{in}}(R_{\text{mid}}) - Y_{\text{out}}(R_{\text{mid}})] \psi(R_{\text{mid}}) = 0$
- Johnson's method (1978):
Non-trivial solution exists only if determinant $|Y_{\text{in}}(R_{\text{mid}}) - Y_{\text{out}}(R_{\text{mid}})|$ is zero:
search for zeroes of this as a function of energy
- Works well for a few channels but is difficult to implement stably in the many-channel case

$Y_{in}(R_{mid}) - Y_{out}(R_{mid})$ for 1 channel



$|Y_{in}(R_{mid}) = Y_{out}(R_{mid})|$ is an awkward function



Can we do better?

- Reconsider the criterion for continuity at R_{mid} :

$$\text{i.e. } [Y_{\text{in}} (R_{\text{mid}}) - Y_{\text{out}} (R_{\text{mid}})] \psi(R_{\text{mid}}) = 0$$

Thus $\psi(R_{\text{mid}})$ is an eigenvector of $[Y_{\text{in}} (R_{\text{mid}}) - Y_{\text{out}} (R_{\text{mid}})]$ with eigenvalue zero.

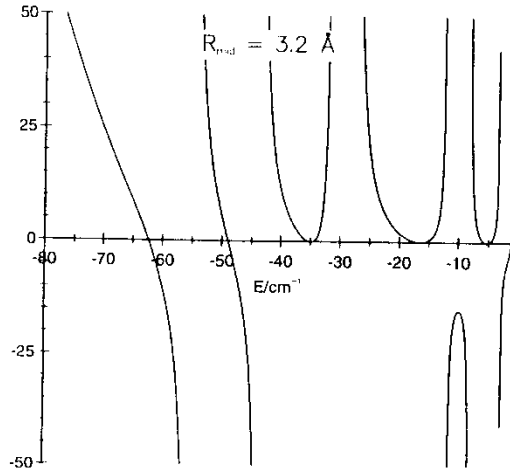
- The individual eigenvalues of

$$[Y_{\text{in}} (R_{\text{mid}}) - Y_{\text{out}} (R_{\text{mid}})]$$

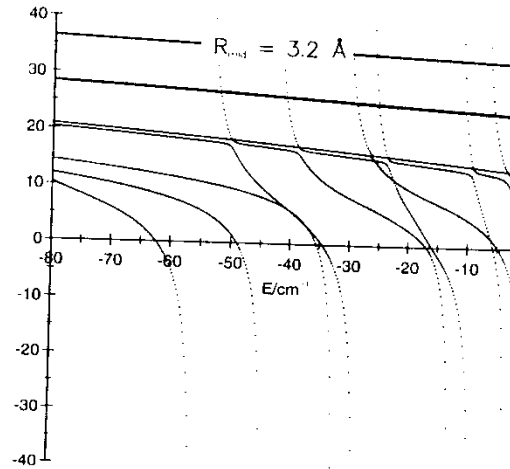
are much better behaved functions than its determinant

Determinant and eigenvalues of matching matrix

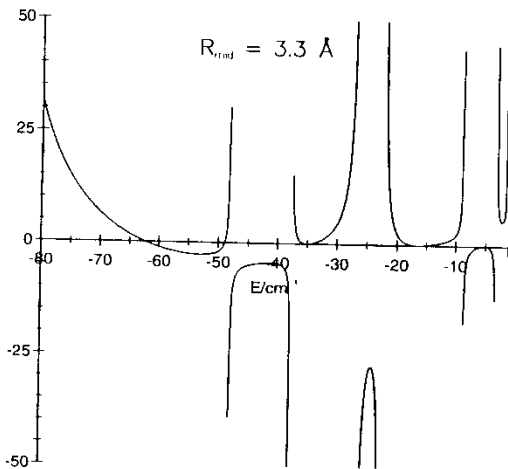
$|Y^* - Y^{-1}|$



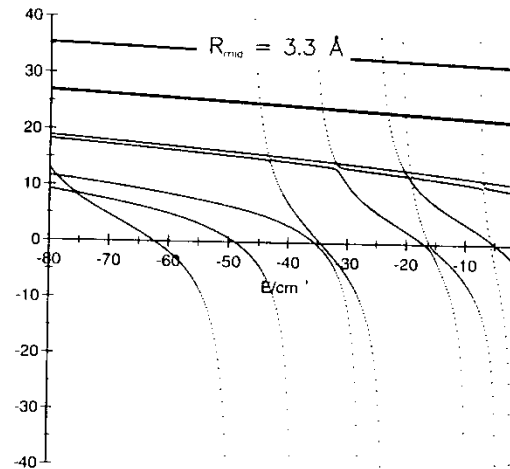
eigenvalues



$|Y^* - Y^{-1}|$



eigenvalues



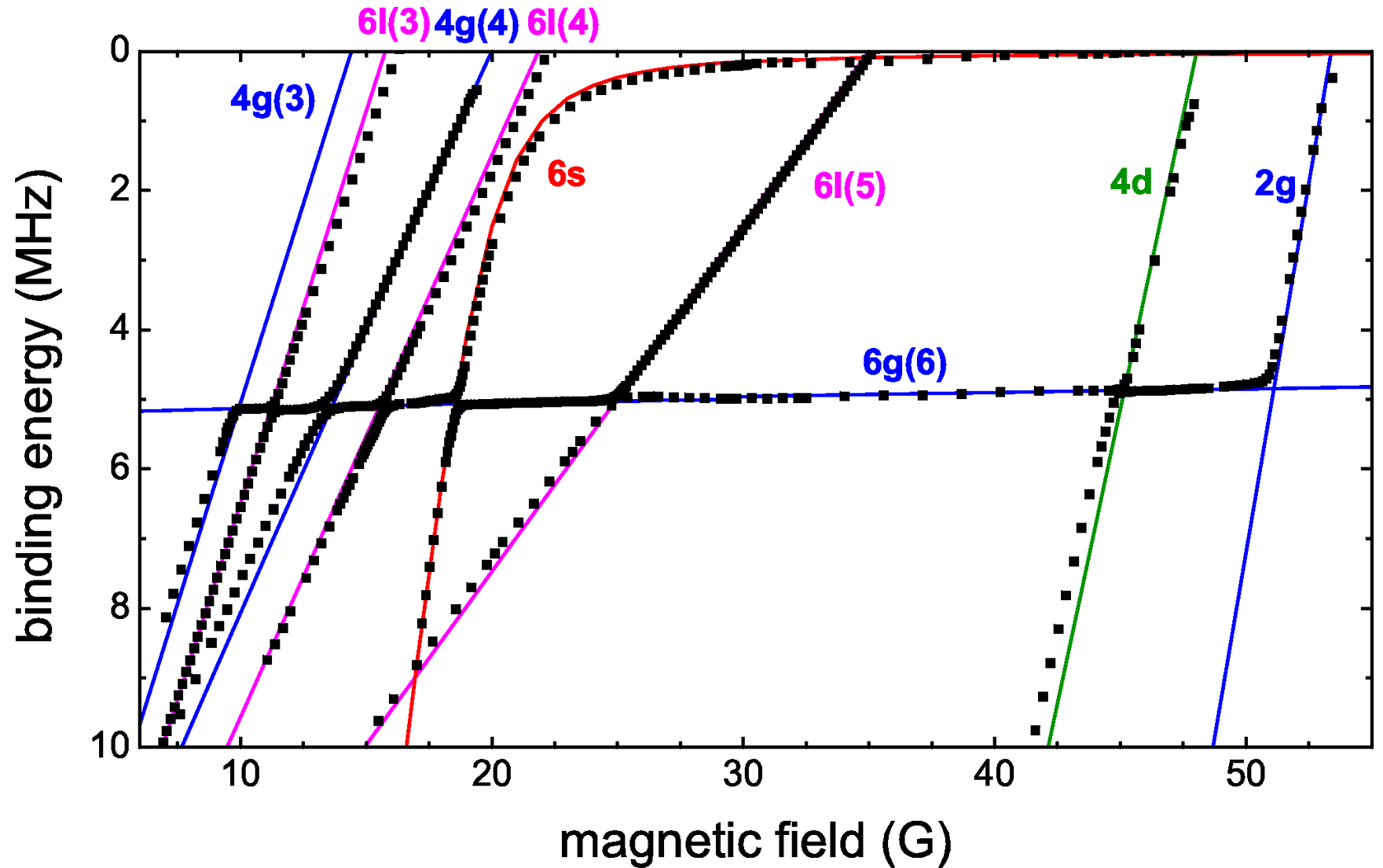
A better approach

- Improved algorithm is to search for zeroes of *smallest eigenvalue* y_{smallest} of matching determinant
- Assisted by node count algorithm (Johnson, 1978).
Generalized node count $n(E)$ is number of eigenvalues below energy (of Schrödinger equation) below energy E :
increments by 1 at each energy where a solution exists.
 $n(E)$ is easily evaluated from a single propagation from R_{min} to R_{max}
- In practice, to locate all the eigenvalues in an energy interval:
 - Use bisection with node count to identify approximate location
 - Use secant convergence to find a zero of $y_{\text{smallest}}(R_{\text{mid}})$
- Calculation of y_{smallest} is extremely stable: easy to get 10-12 digits, even if not converged with respect to step size
- Energy eigenvalues can be converged to almost any desired precision
- It is possible (but not quite so stable) to recover an explicit wavefunction $\psi(R)$ by propagating outwards and inwards from $\psi(R_{\text{mid}})$

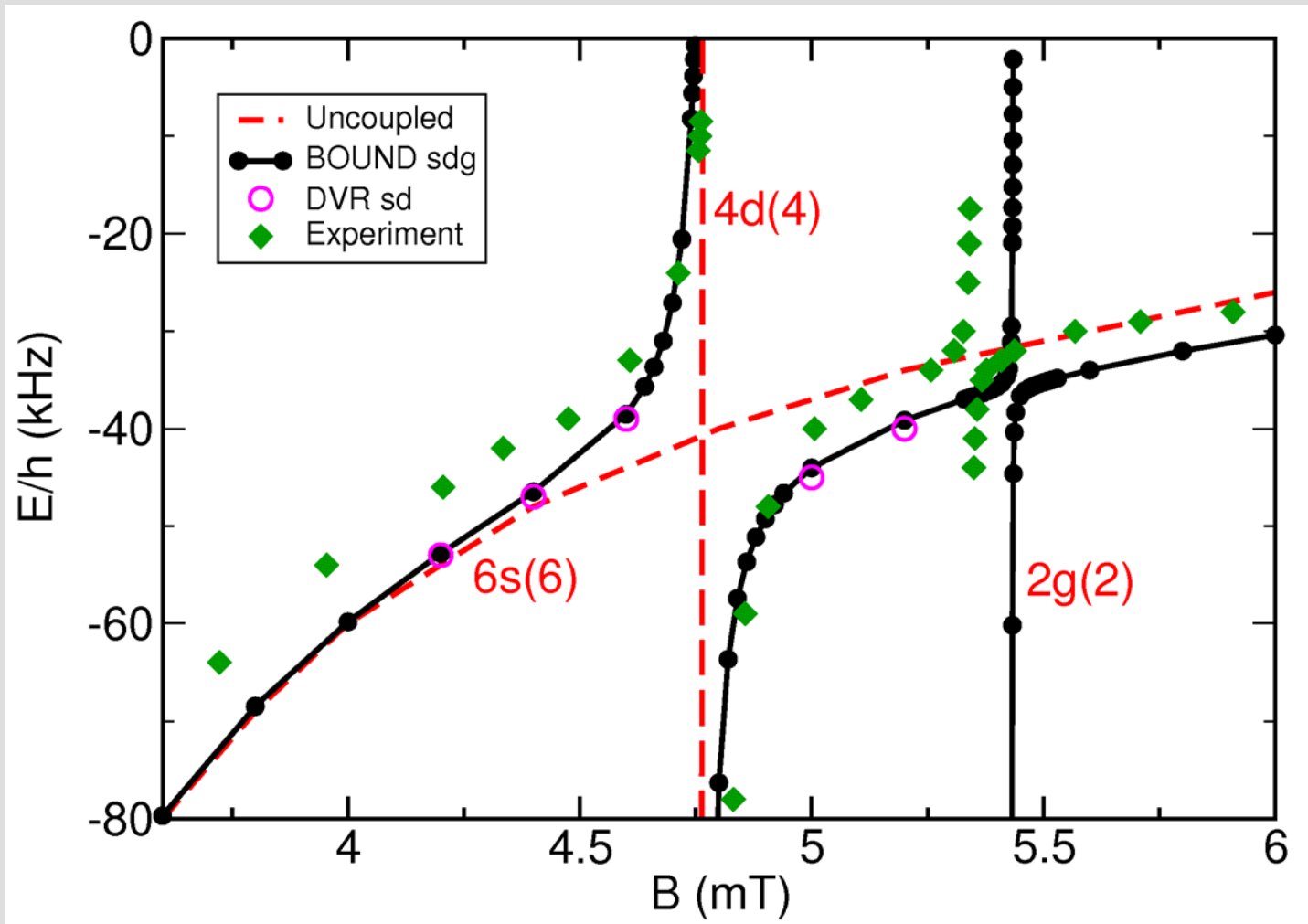
Implementation and Propagators

- Algorithms implemented in BOUND package (Hutson 1983-2010)
- Log-derivative propagators (from embedding methods) are extremely stable even in the presence of deeply closed channels
- Use fixed-step propagators in region of deep well (innermost 1 nm)
very good step-size convergence: $O(h^4)$
Various versions due to Johnson, Manolopoulos
- Stability is good enough to use Richardson extrapolation when needed to extrapolate to zero step size
- Recent development:
 - For weakly bound states we need to propagate to very long range
 - Airy-function-based propagator of Alexander can take extremely long steps in long-range region:
typically only 5% of time to go out to 1 to 10 μm if needed
 - Adaptive step-size algorithm used by Airy propagator needed some modification for inwards propagation
(decreasing rather than increasing step size)

Overview of Cs_2 levels in top 10 MHz (10^{-7} of well depth) as function of magnetic field (Innsbruck experiments)

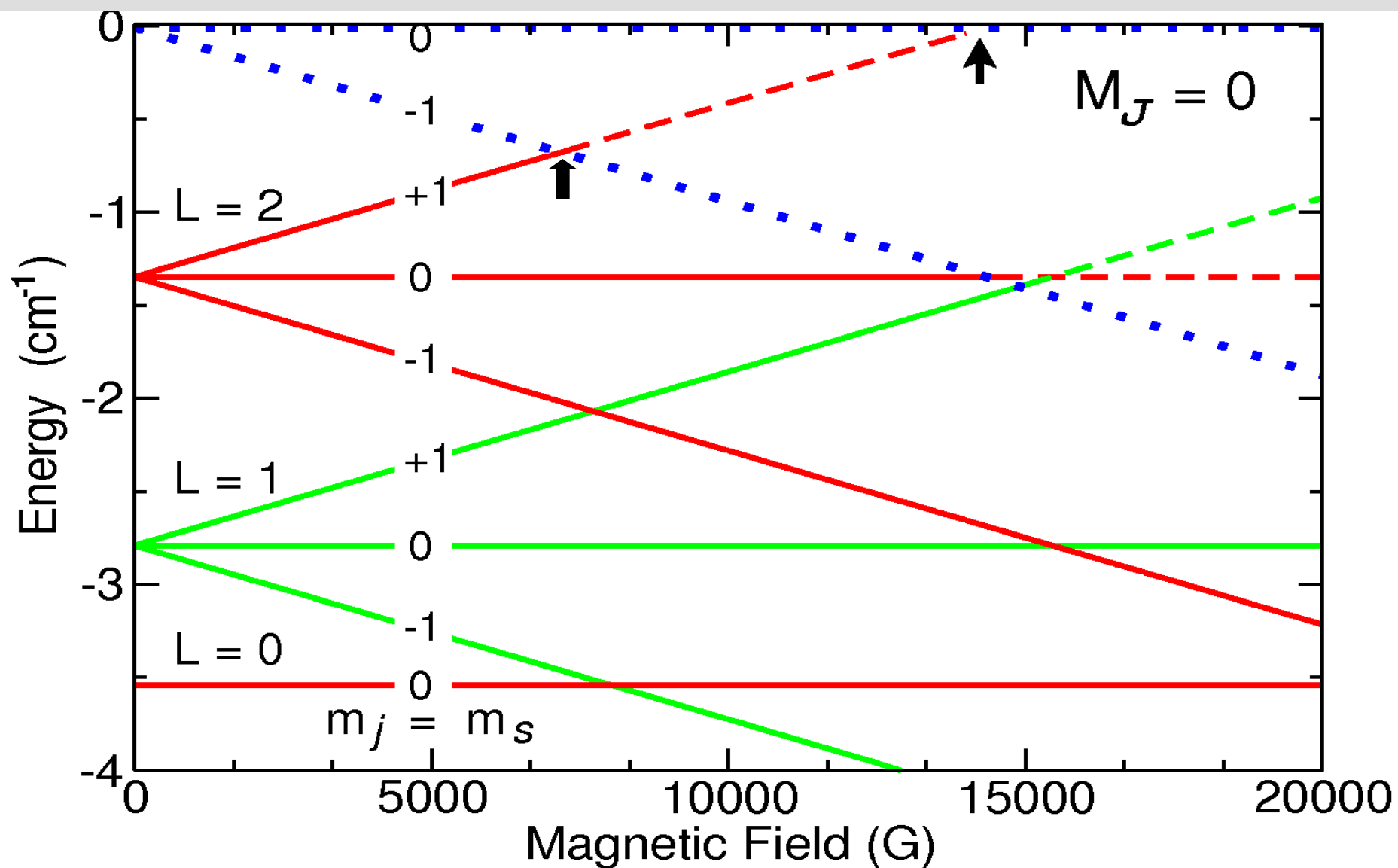


Cs_2 : focus on top 50 kHz (5×10^{-9} of well depth)



Remaining discrepancies are due to deficiencies in potentials

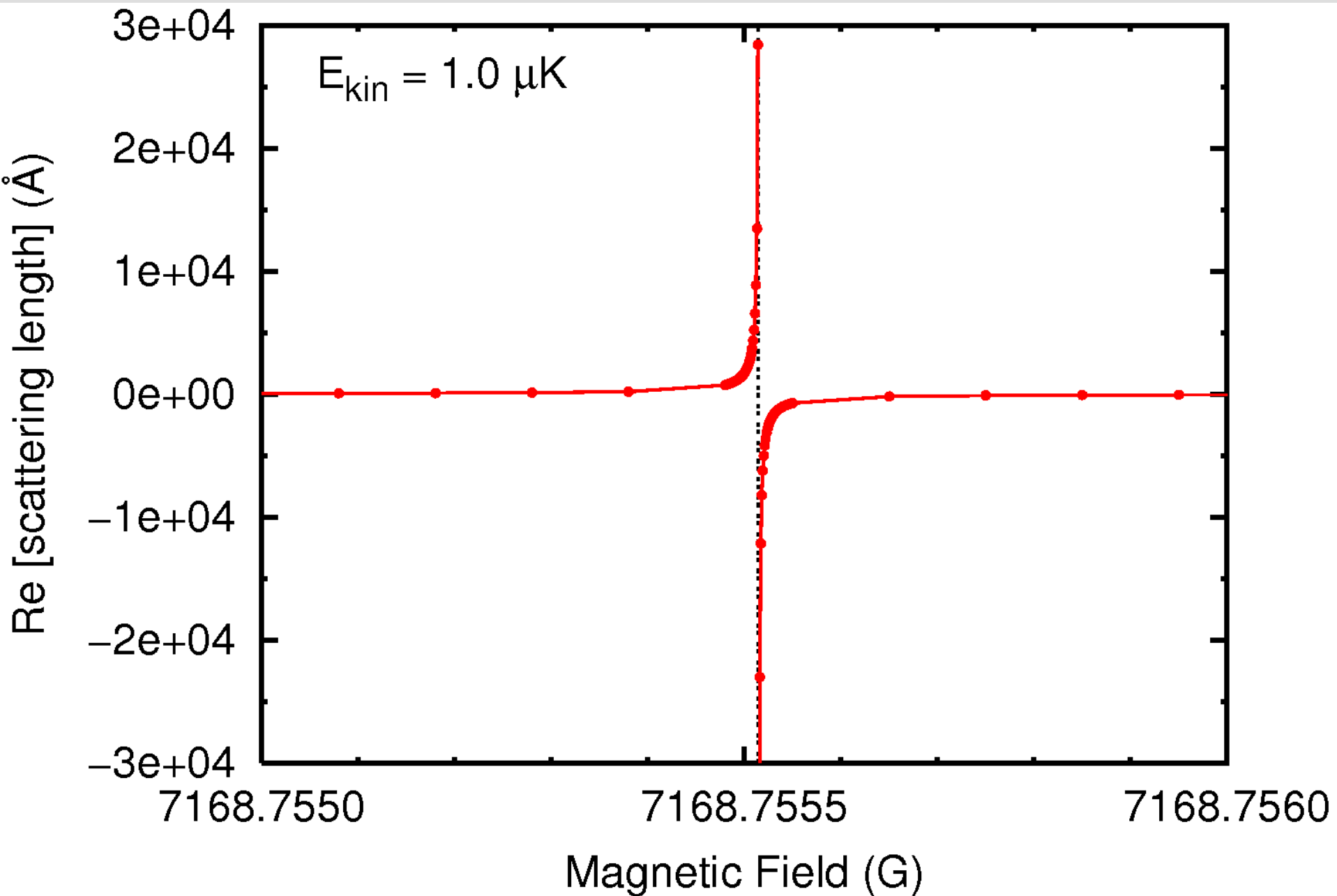
Molecular example: states crossing threshold in $^3\text{He} + \text{NH}$



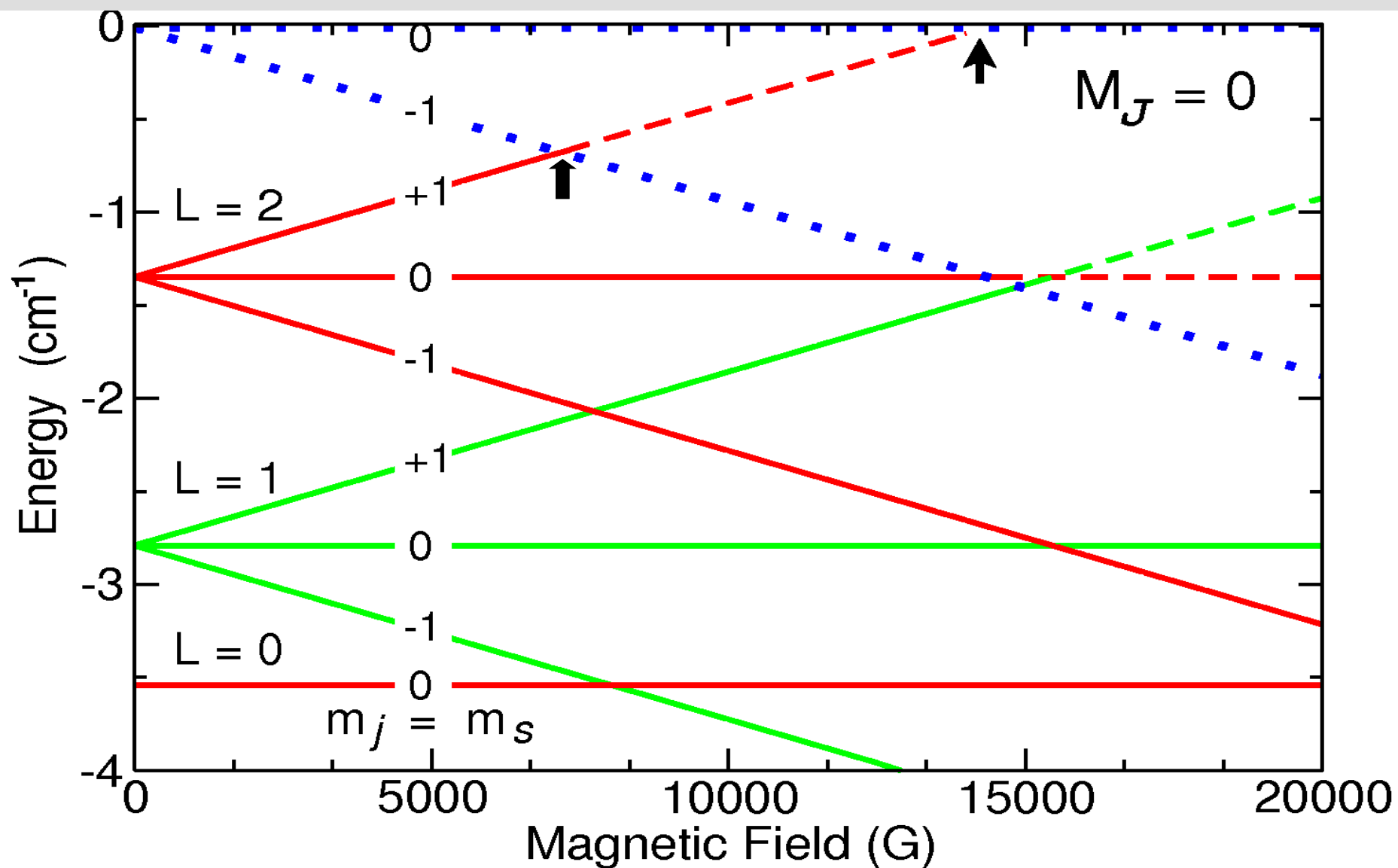
Bound states: red and green; thresholds: blue dots

Resonances expected at 7169 G and 14340 G

He+NH scattering resonance 1: pole in scattering length



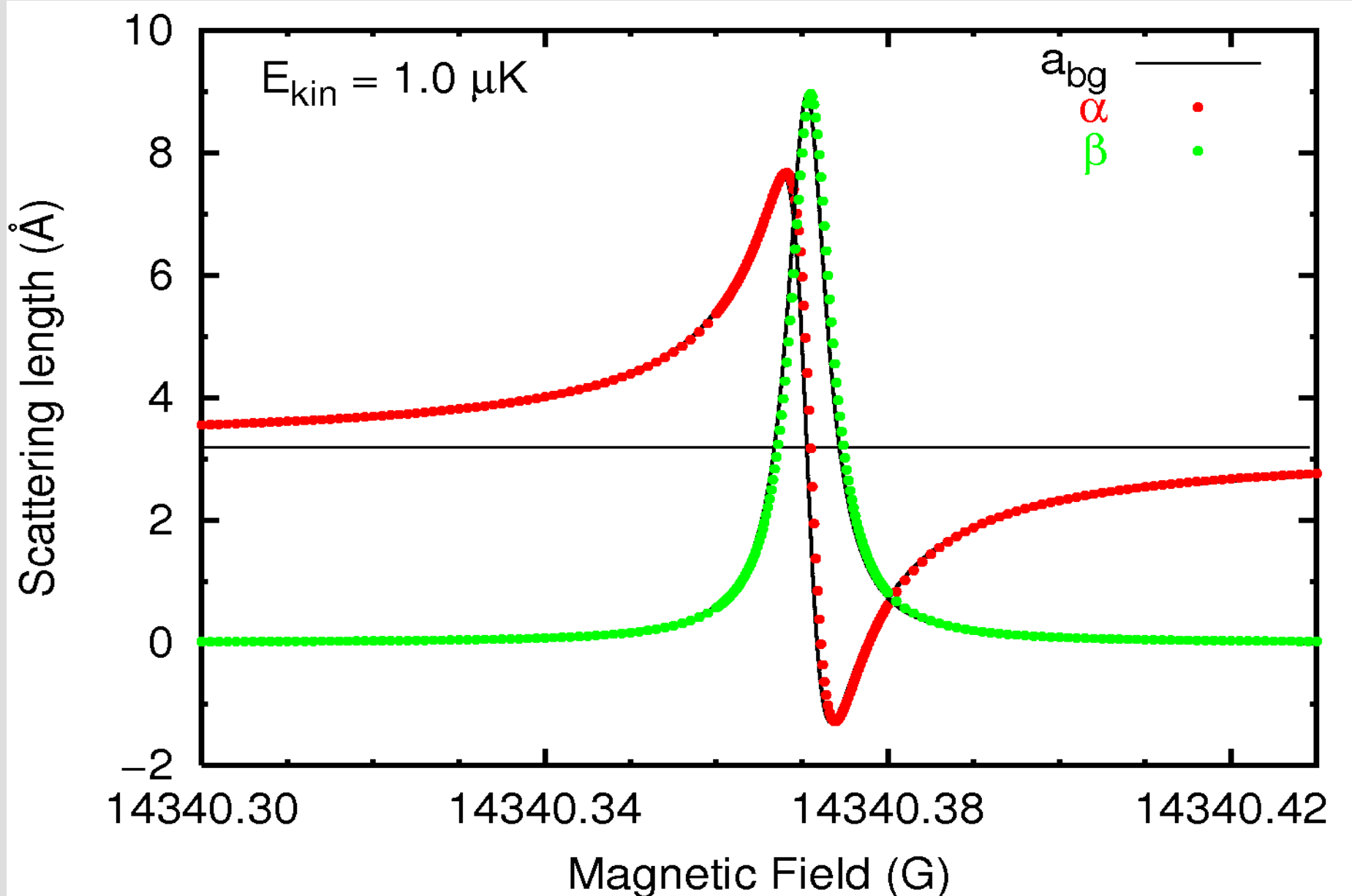
Molecular example: states crossing threshold in $^3\text{He} + \text{NH}$



Bound states: red and green; thresholds: blue dots

Resonances expected at 7169 G and 14340 G

He+NH scattering resonance 2:
Re(a) shows small oscillation, *not* pole; $-\text{Im}(a)$ shows peak



Threshold behaviour

- Convenient to define complex k -dependent scattering length $a(k)$, related to phase shift $\delta(k)$ by

$$a(k) = \alpha(k) - i\beta(k) = \frac{-\tan \delta(k)}{k} = \frac{1}{ik} \left(\frac{1 - S_{00}}{1 + S_{00}} \right)$$

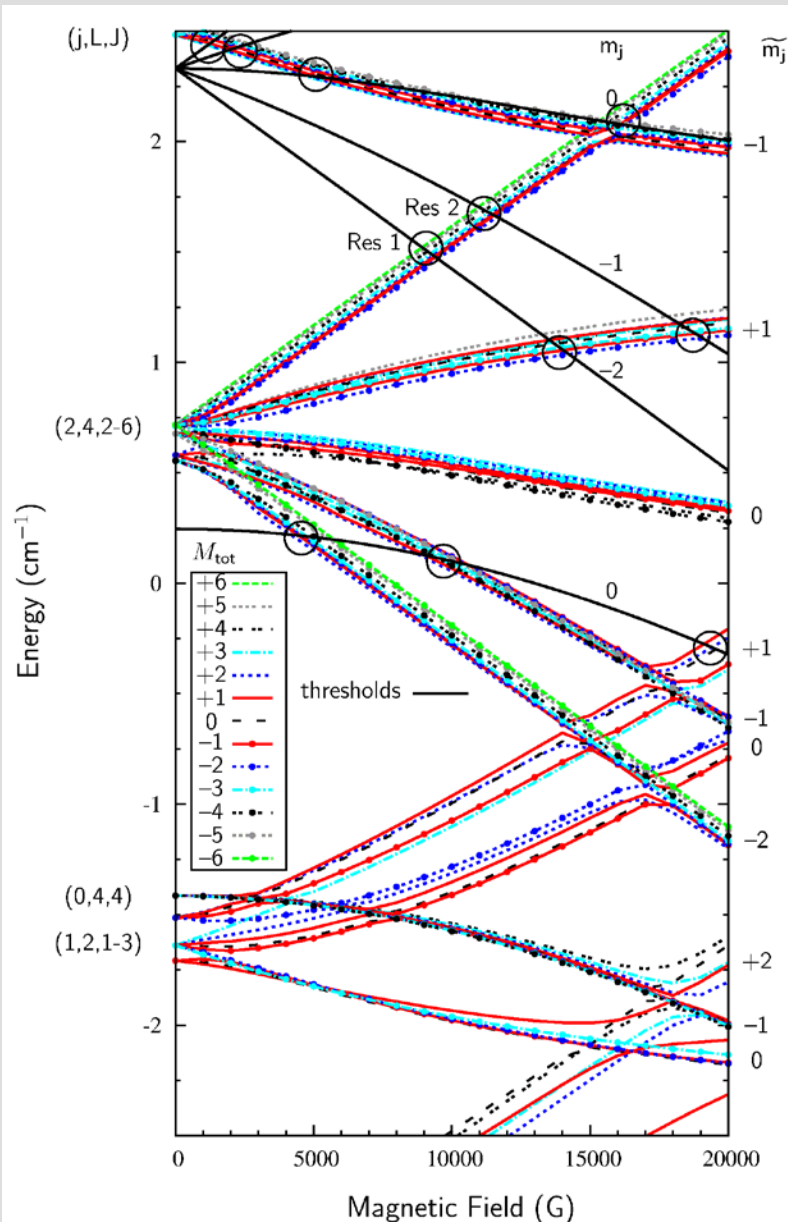
S -wave cross sections given *exactly* by $\sigma_{el}(k) = 4\pi |a|^2 / (1 + k^2 |a|^2 + 2k\beta)$
 $\sigma_{inel}(k) = 4\pi\beta / [k(1 + k^2 |a|^2 + 2k\beta)]$

- Across a resonance, elastic S -matrix element S_{00} describes a circle in the complex plane:
In presence of inelastic scattering, radius of circle is proportional to wavenumber k with $E_{kin} = \hbar^2 k^2 / 2\mu$
- Complex scattering length across resonance is

$$a(B) = a_{bg} + \frac{a_{res}}{2(B - B_{res})/\Gamma^{inel} + i}$$

"Resonant scattering length" $a_{res} = 2\gamma_0/\Gamma^{inel}$ may be small.

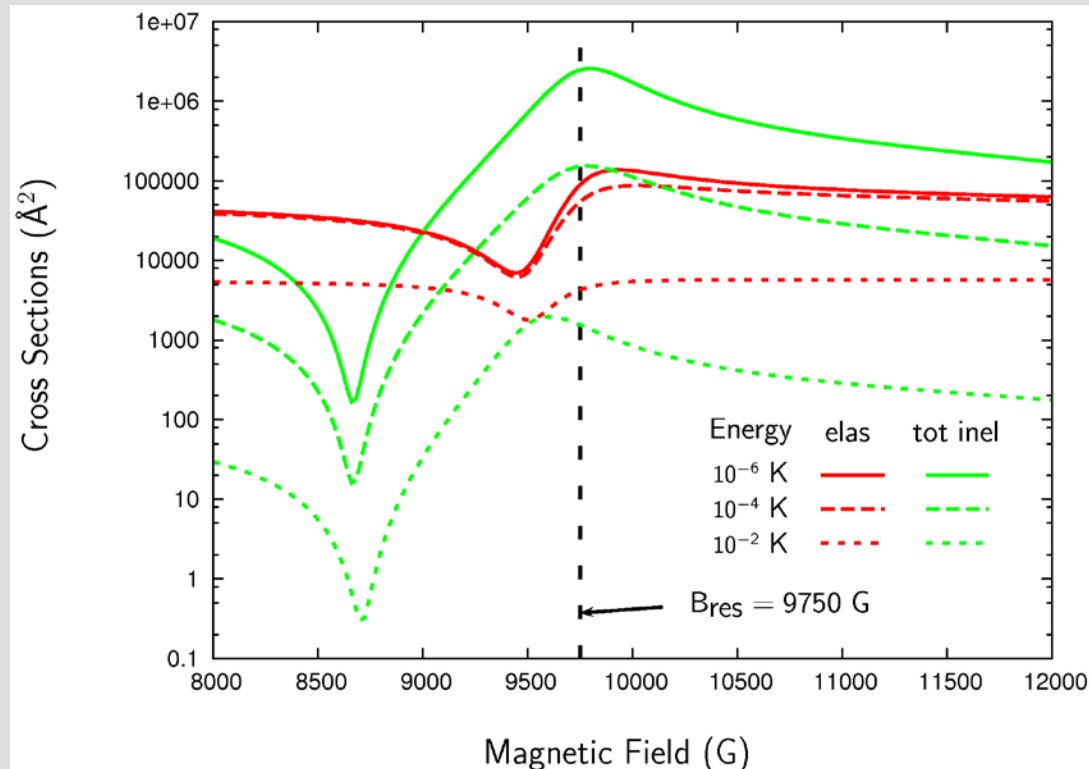
A more strongly inelastic example: He + O₂



- Ground state of O₂ is $^3\Sigma_g^-$, with electron spin $s=1$.
- Lowest rotational state for $^{16}\text{O}_2$ is $n=1$, not $n=0$.
- Binding energy much shallower than for Cs_2
- Complicated pattern of He-O₂ levels crossing O₂ thresholds (black)
- Note "bound" levels continued above lowest threshold by box quantisation
- Locations of Feshbach resonances shown by circles

Feshbach resonances in He + O₂

- He + O₂ collisions show strong inelasticity (M-changing collisions)
- Elastic and inelastic cross sections exhibit asymmetric lineshapes that may have very deep troughs
- For He+O₂ the inelasticity can be suppressed by a factor of 1000 over a wide range of fields and temperatures near resonance
- Scattering length follows same formula but characterised by *complex* a_{res}



PRL 103, 163201 (2009).

Conclusions

- Bound states formed from ultracold molecules offer important new possibilities for quantum control
- There are complicated networks of bound states with many interactions and avoided crossings as a function of applied field
- Propagation methods have major computational advantages over methods that use radial basis sets
- Feshbach resonances do *not* always produce poles in scattering length:
Inelastic scattering can strongly suppress resonant peaks in scattering lengths and cross sections
- For some systems, inelastic collisions can be strongly suppressed near Feshbach resonances

Who did what, and where can I find it?

- BOUND code: contact J.M.Hutson@durham.ac.uk
 - Methods used in BOUND: *Comp. Phys. Commun.* 84, 1 (1994).
 - Extension to very long-range states:
PRA 78, 052703 (2008) (with Paul Julienne and Eite Tiesinga)
- Suppression of poles in scattering resonances:
 - Formal theory: *New J. Phys.* 9, 152 (2007)
 - He + NH application, *PRA* 75, 022702 (2007)
with Maykel Leonardo González-Martínez (Cuba)
- Asymmetric lineshapes and suppression of inelasticity:
 - *PRL* 103, 163201 (2009) (with Musie Beyene and MLGM)
- Recent reviews on alkali metal dimers:
 - Molecule formation in ultracold atomic gases,
Int. Rev. Phys. Chem. 25, 497 (2006)
 - Molecular collisions in ultracold atomic gases,
Int. Rev. Phys. Chem. 26, 1 (2007);
[arXiv:physics/0610219](https://arxiv.org/abs/physics/0610219)