# Introduction to ultracold molecules

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# Introduction to ultracold molecules

1. Properties, applications and production
2. Internal state control and trapping molecules
3. Controlling molecular motion and collisions

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# Introduction to ultracold molecules

## 1. Properties, applications and production

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# Why ultracold polar molecules?

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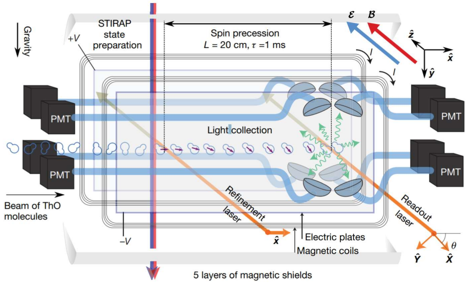
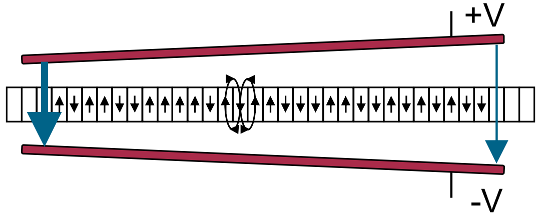
## Precision measurement




The ACME collaboration, Nature **562**, 355 (2018)

## Quantum computation

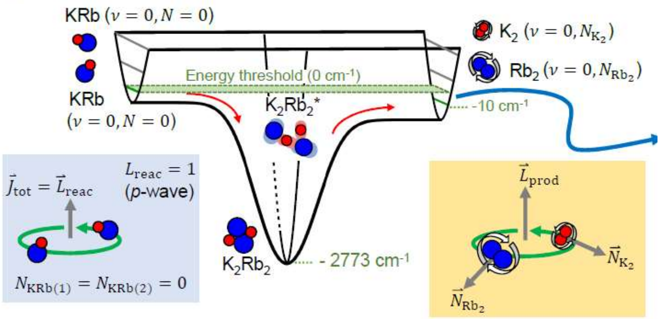



DeMille, PRL **88**, 067901 (2002)

## Novel quantum fluids

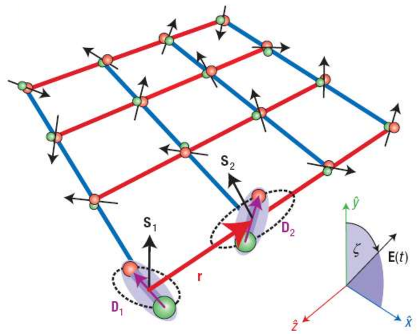
Schmidt, PRR **4**, 013235 (2022)

## Ultracold Chemistry




Liu, Nat. Phys. **16**, 1132 (2020)

## Quantum simulation

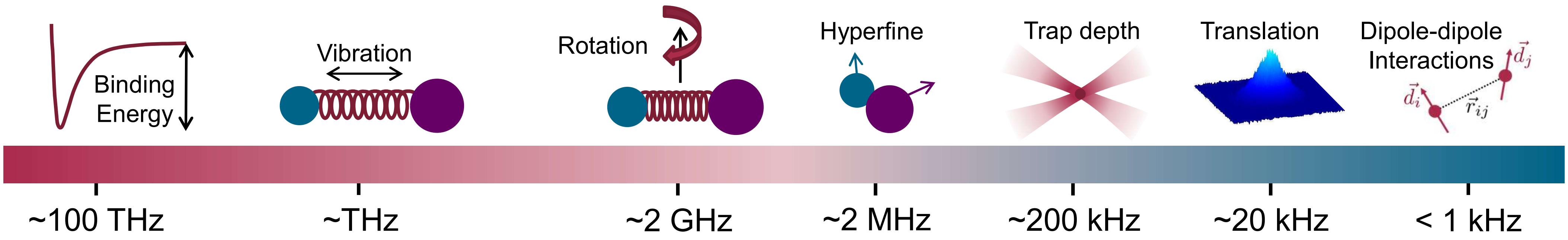



Micheli, Nat. Phys. **2**, 341 (2006)

# Rich internal structure

Durham University

Adapted from Jin/Ye
Physics Today 2011



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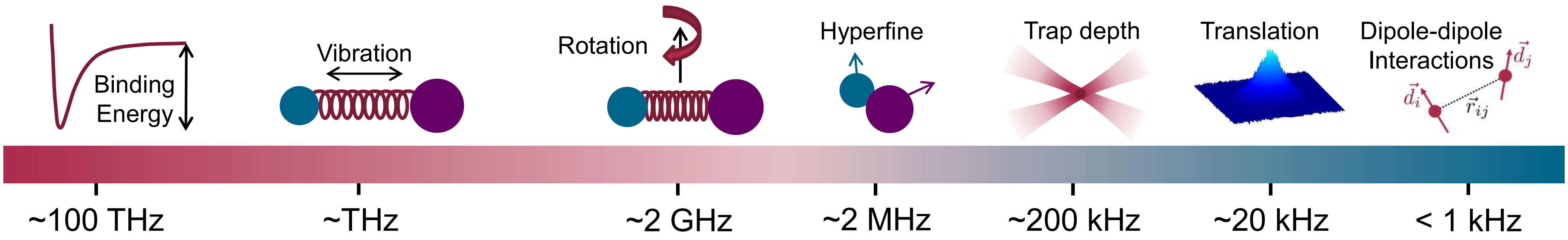
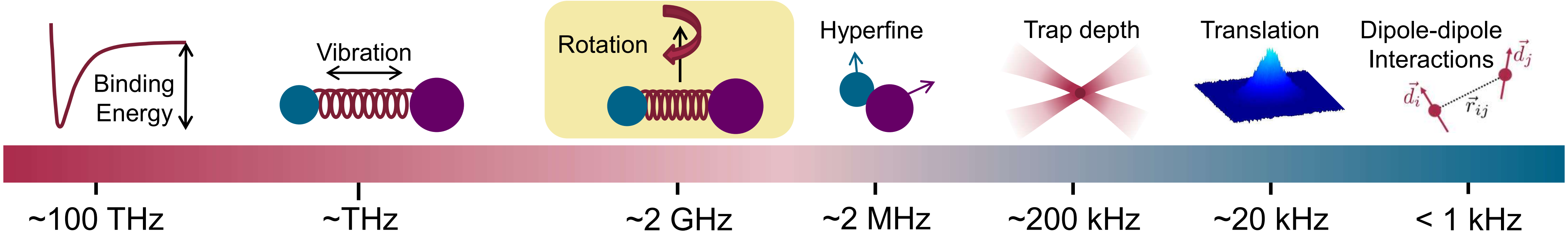
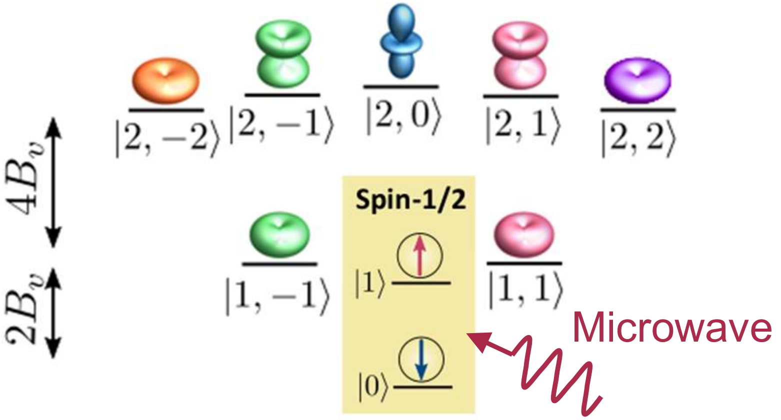


# Rich internal structure




Ladder of long-lived rotational states

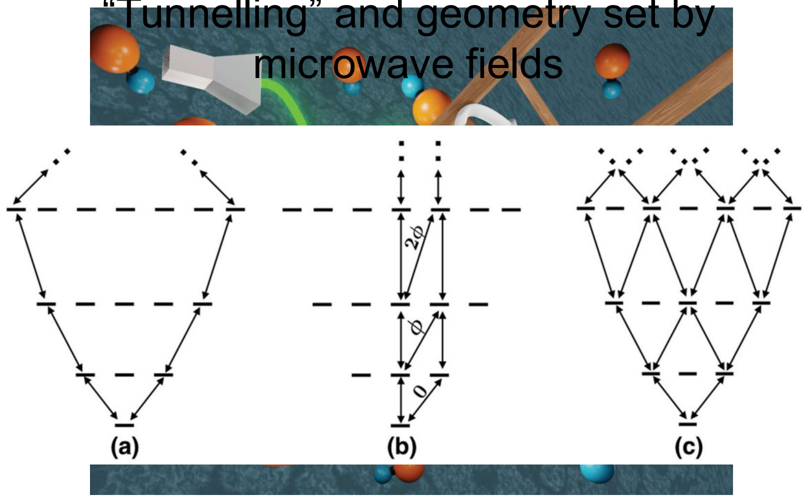
$$E_N = B_v N(N+1)$$




Encode and manipulate spins

Blackmore et al., Phys. Chem. Chem. Phys. 22, 27529 (2020)

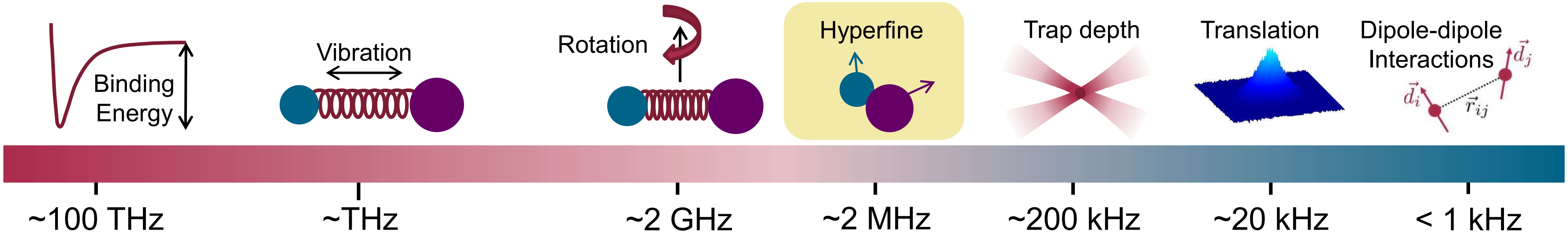
"Tunnelling" and geometry set by microwave fields




Engineering synthetic dimensions

Sundar et al., Scientific Reports 8, 3422 (2022)

# Rich internal structure

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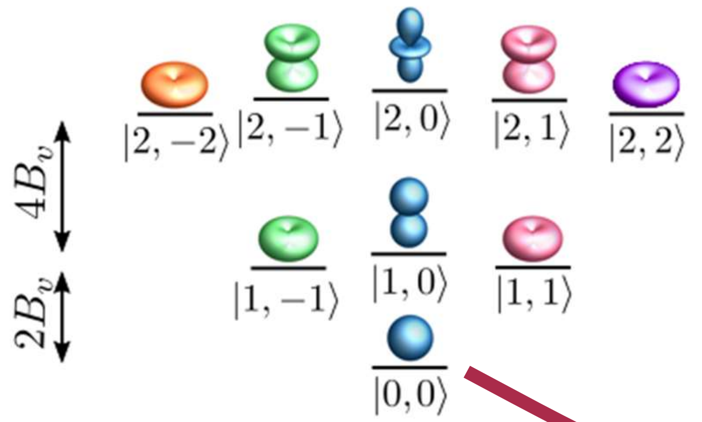
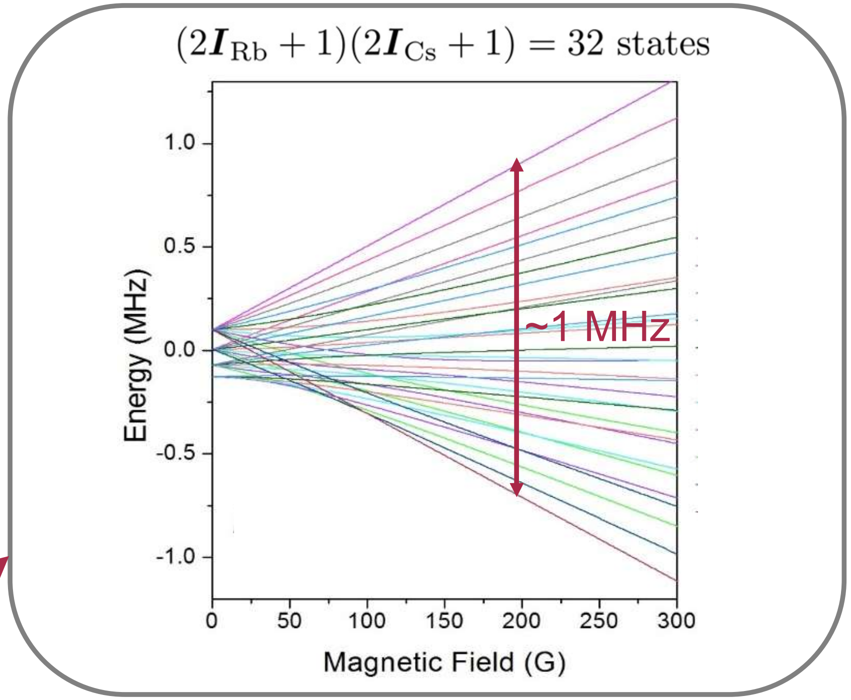
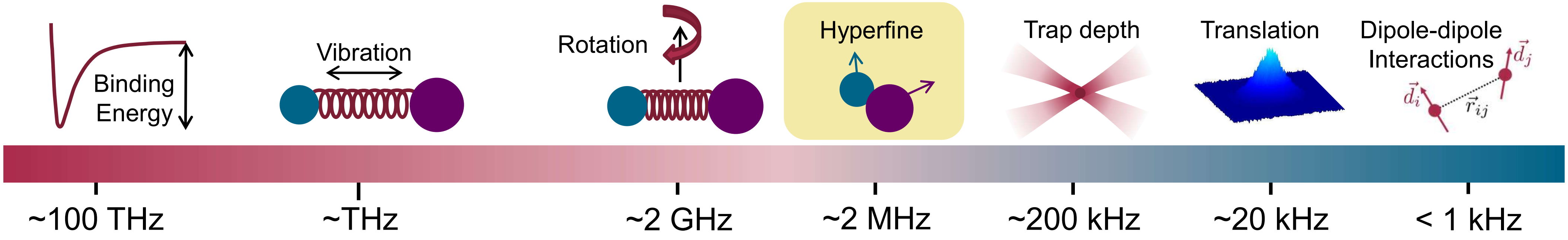
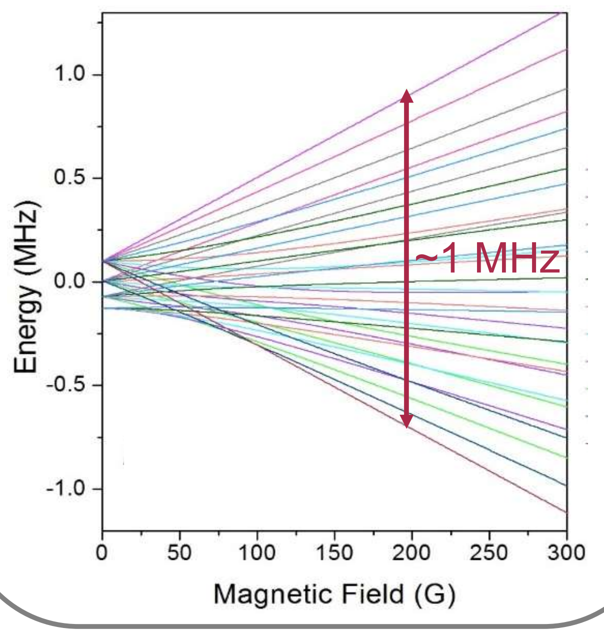


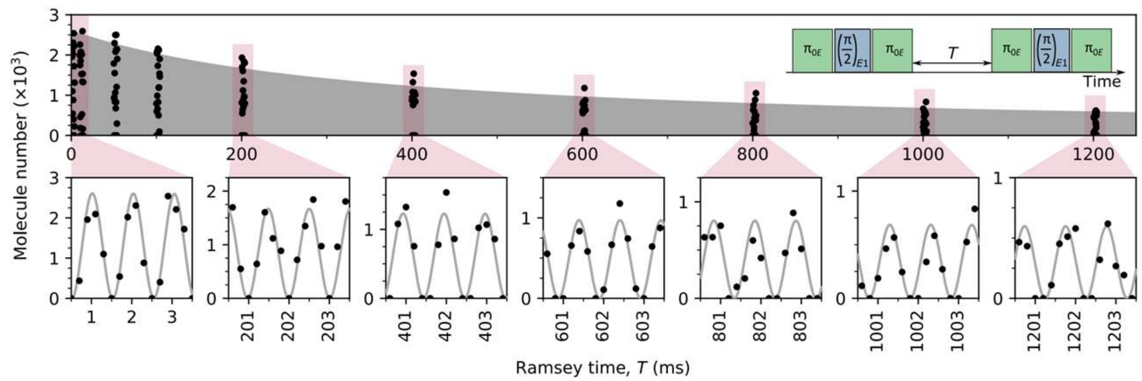
# Rich internal structure





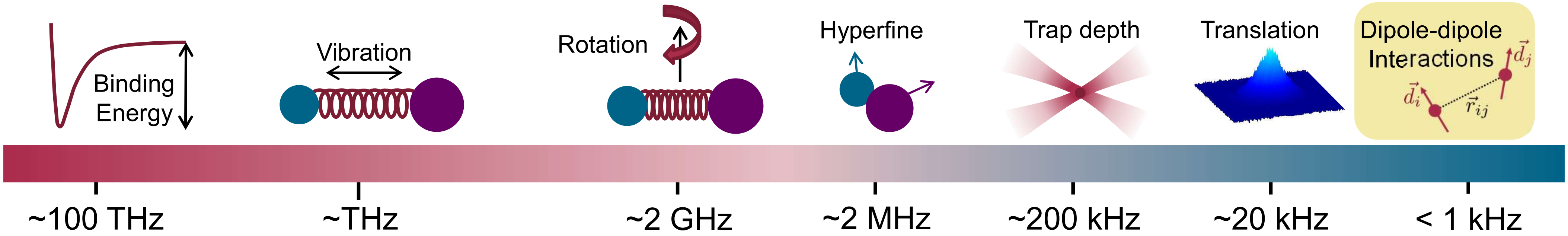

"Robust storage qubits in ultracold polar molecules"
Gregory et al., Nature Physics 17, 1149 (2021)



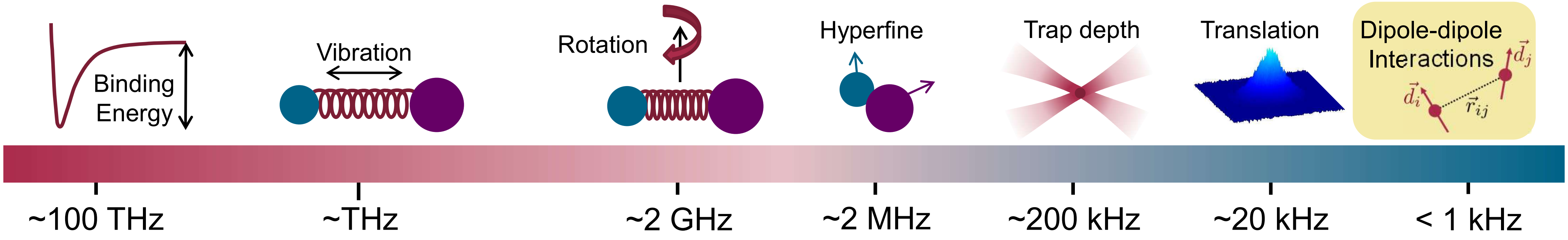

Coherence time > 5.6 seconds (95% confidence)

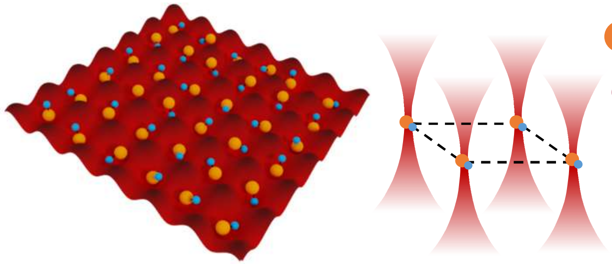
Also: Park et al., Science 357, 372-375 (2017)
Lin et al., PRL 128, 223201 (2022)

# Rich internal structure



# Rich internal structure



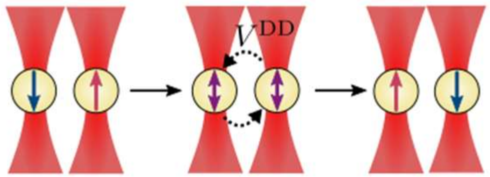




$$H_{XXZ} = \sum_{i \neq j} \left[ \frac{J_\perp}{2} (S_i^+ S_j^- + S_i^- S_j^+) + J_z S_i^z S_j^z \right]$$

"Quantum Computation and Quantum Simulation with Ultracold Molecules"
Nature Physics **20**, 730-740 (2024)

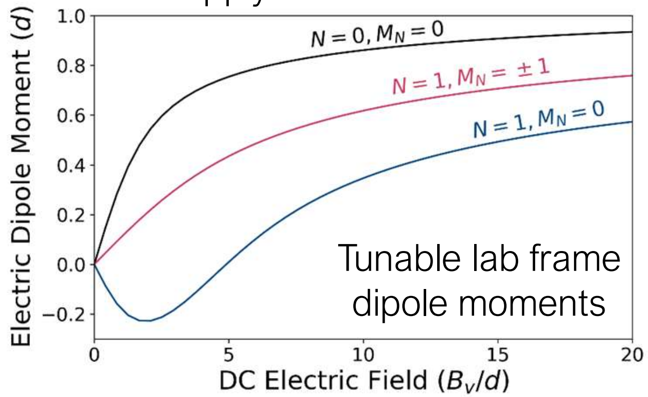
## Controllable dipole-dipole interactions

Via transition dipole moment between rotational states




Spin-exchange interactions

Apply an electric field




Or mix states with microwave fields (coherent superpositions / dressing)

**Challenge: quantum control of internal and external degrees of freedom of molecules**

# Opportunities and challenges

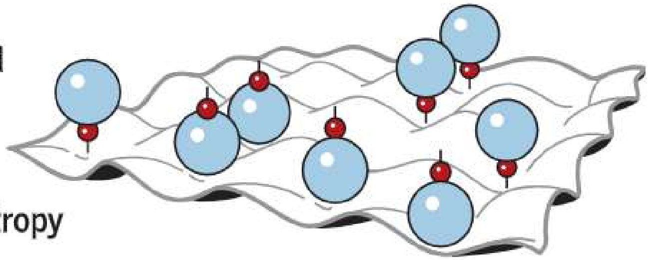
**Pinned two-level molecules**

XXZ spin model

Spin liquids

Many-body localization and transport

**Control of E-fields**
**Higher fillings and low entropy**
**Addressability**



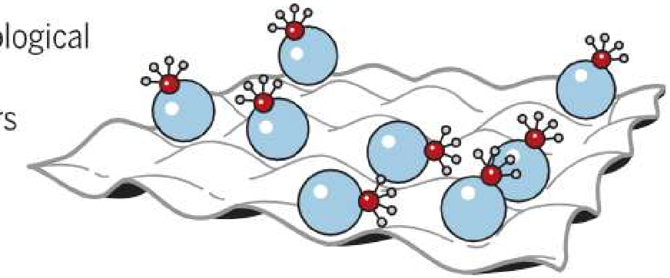
**Pinned multi-level molecules**

Spin-orbit coupling

Symmetry protected topological phases

Fractional Chern insulators

**Control of microwaves**
**Local dressing**



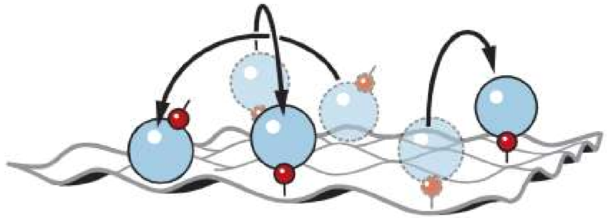
**Mobile molecules**

Topological superfluids

t-J models

Dipolar chains and clusters

**Efficient cooling**
**Control of chemistry**



"Cold molecules: Progress in quantum engineering of chemistry and quantum matter" Science **357**, 1002-1010 (2017)

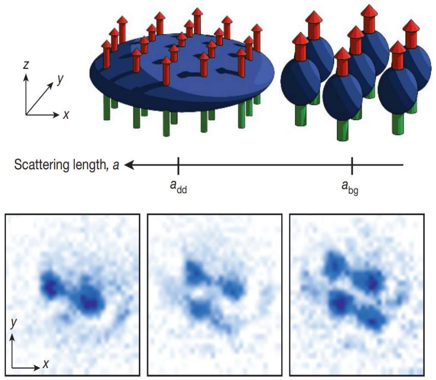
**Challenge: quantum control of internal and external degrees of freedom of molecules**

# Dipoles and dipolar interactions

# Aside: Ultracold Dipolar Systems

**Highly Magnetic Atoms**

Weak dipoles
~10μ$_B$, stable (10s)

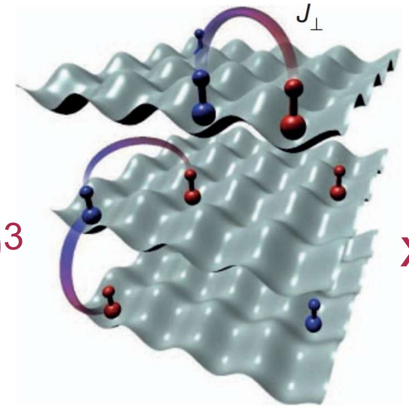



Kadau *et al.*,
Nature **530**, 194 (2016)

x $10^3$

**Polar Molecules**

Medium dipoles
3 Debye, stable* (10s)

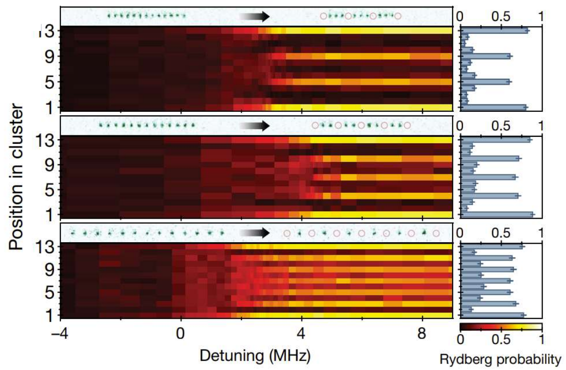



Yan *et al.*,
Nature **501**, 521 (2013)

x $10^3$

**Rydberg Atoms**

Strong dipoles
$10^4$ Debye, lifetime ~100μs




Bernien *et al.*,
Nature **551**, 579 (2017)

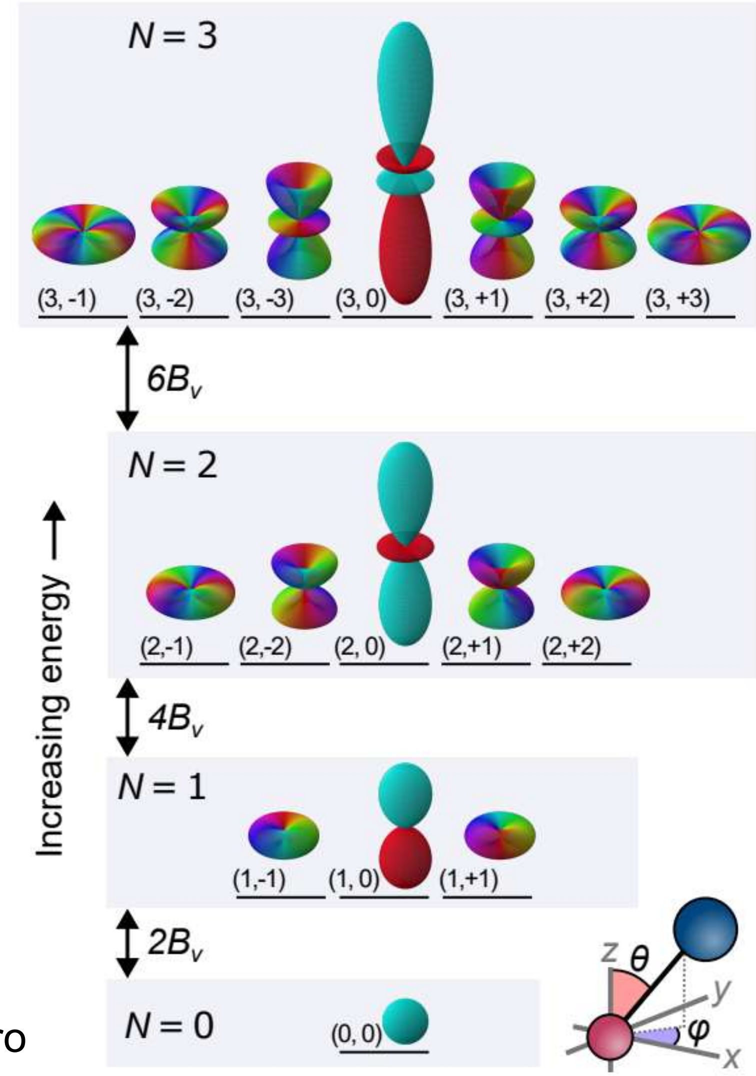
**Mobile Dipoles** → **Fixed Dipoles**

* Isolated molecules
Collisions require shielding

# ‘Permanent’ molecular dipoles

Electric dipole moment results from uneven sharing of electrons
For a simple diatomic, it points along the internuclear axis
Well defined in the ***molecular frame***
But often ***zero in the lab frame!***

Orientation in the lab frame dictated by rotational wavefunctions




Rigid rotor model:

$$H_{\text{rot}} = B_v \boldsymbol{N}^2$$

$$U_{\text{rot}} = B_v N(N+1)$$

$$\psi = Y_{N,M_N}(\theta, \phi)$$

No defined orientation in lab frame
For molecules in eigenstates of rotation, lab-frame dipole moment is zero

# Engineering lab frame dipole moments with dc fields

Orient the molecule in the lab frame with a dc electric field

$$H_{\mathrm{dc}} = -d\boldsymbol{E}\cdot\hat{\boldsymbol{n}} = -dE\cos\theta$$

Where $\theta$ is the angle between the internuclear axis and the electric field applied along *z*

In the presence of rotation leads to matrix elements of the form

$$\langle N, M_N|\, H_{\mathrm{dc}}\,|N', M_N'\rangle = -dE\sqrt{(2N+1)(2N'+1)}(-1)^{M_N} \times \begin{pmatrix} N & 1 & N' \\ -M_N & 0 & M_N' \end{pmatrix}\begin{pmatrix} N & 1 & N' \\ 0 & 0 & 0 \end{pmatrix}$$

Wigner-3j symbols mean that the electric field mixes states that differ in $N$ by 1 and have the same value of $M_N$

Combining with $H_{\mathrm{rot}}$ we can visualise the matrix elements for $N$ = 0 and 1 (note need diagonalise full matrix)

$$\langle N, M_N|\, H\,|N', M_N'\rangle =$$

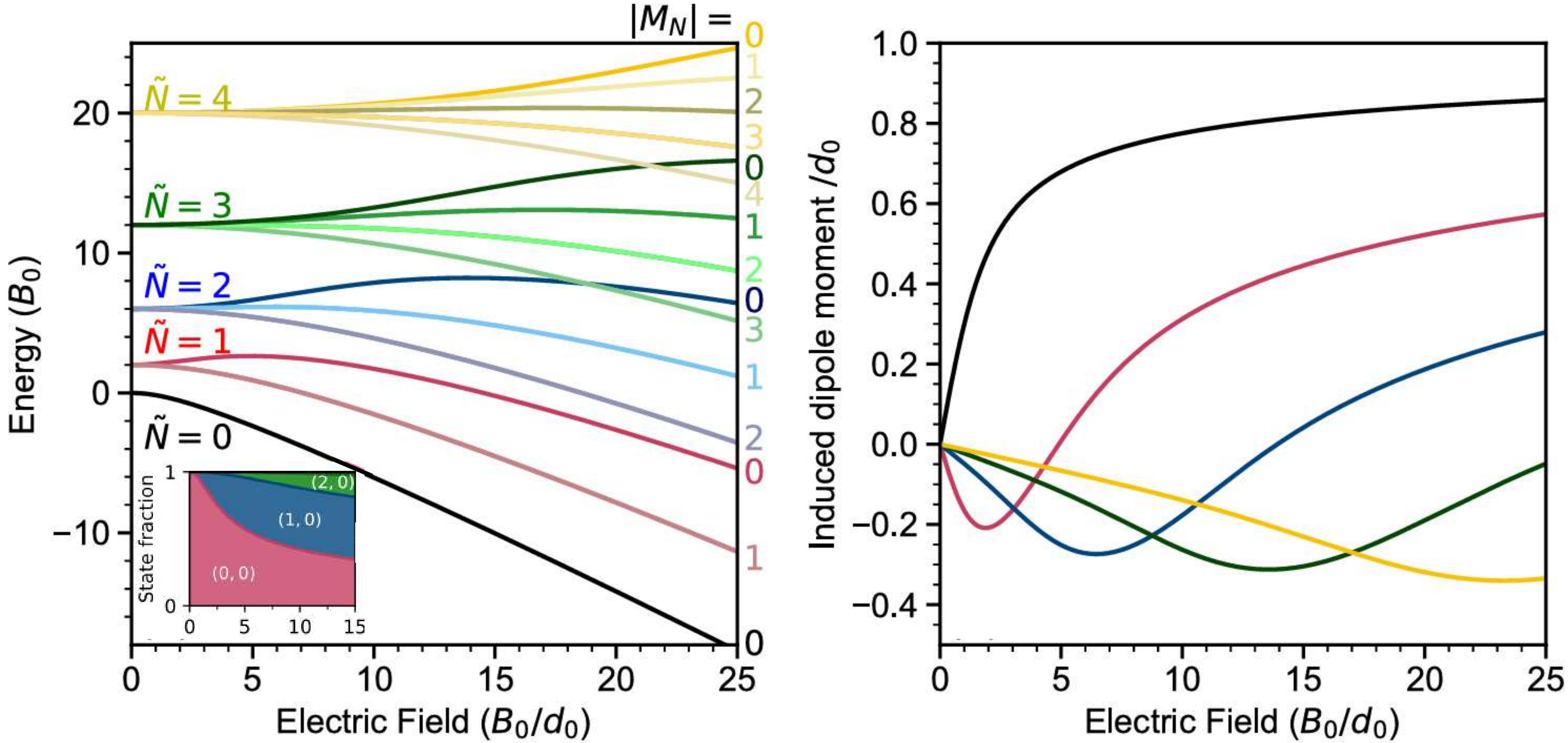
$$\begin{array}{cccc|l} \langle 0,0| & \langle 1,+1| & \langle 1,0| & \langle 1,-1| & \\ 0 & 0 & -dE/\sqrt{3} & 0 & |0,0\rangle \\ 0 & 2B_v & 0 & 0 & |1,+1\rangle \\ -dE/\sqrt{3} & 0 & 2B_v & 0 & |1,0\rangle \\ 0 & 0 & 0 & 2B_v & |1,-1\rangle \end{array}$$

The effect of the mixing depends on size of $dE$ compared to $B_v$

Natural unit of $E$ is $B_v\,/\,d_0$

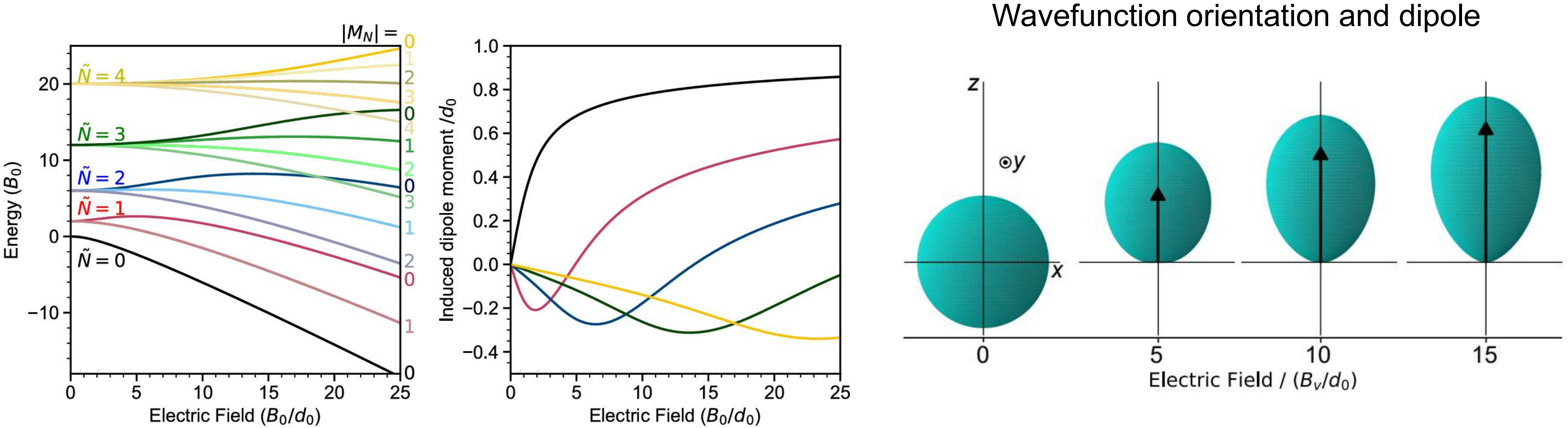
# Engineering lab frame dipole moments with dc fields

What does this look like?



# Engineering lab frame dipole moments with dc fields

What does this look like?




Now have static dipoles whose orientation is controlled by the direction of the dc electric field

By extension – can also mix states and produce dipoles using ac electric fields

# Inducing dipoles with microwave dressing

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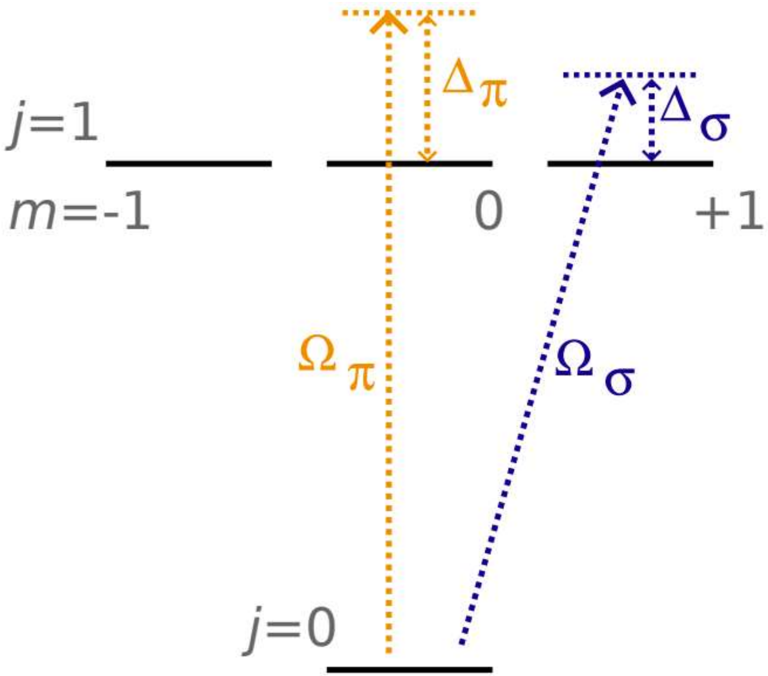
Preparing molecules in dressed state produces dipoles oscillating at the microwave frequency




For linear $\pi$ polarisation

$$d_{\text{eff}} = \frac{d_0}{\sqrt{3[1+(\Delta/\Omega)^2]}}$$

For circular $\sigma$+ polarisation

$$d_{\text{eff}} = \frac{d_0}{\sqrt{6[1+(\Delta/\Omega)^2]}}$$

Detuning and Rabi frequency control interactions

Important for shielding molecular collisions

Karman et al., PRA **105**, 013321 (2022)
Schindewolf et al., arXiv:2512.14511

# Comparing molecules

Durham University

| Species | Dipole (D) | $2B_{rot}$ / h (GHz) | Critical E-field (V/cm) |
|---|---|---|---|
| NaLi | 0.463 | 22.8 | 48875 |
| LiK | 3.45 | 15.6 | 4488 |
| LiRb | 4 | 13.2 | 3275 |
| LiCs | 5.52 | 11.6 | 2086 |
| NaK | 2.72 | 5.64 | 2058 |
| NaRb | 3.1 | 4.18 | 1338 |
| NaCs | 4.75 | 3.56 | 744 |
| KRb | 0.574 | 2.23 | 3856 |
| KCs | 1.906 | 1.86 | 969 |
| RbCs | 1.2 | 0.98 | 811 |
| CaF | 3.07 | 10.27 | 3320 |

Rotational constant
$\propto$ 1/(Moment of inertia)

Moment of inertia
$I = \mu r^2$

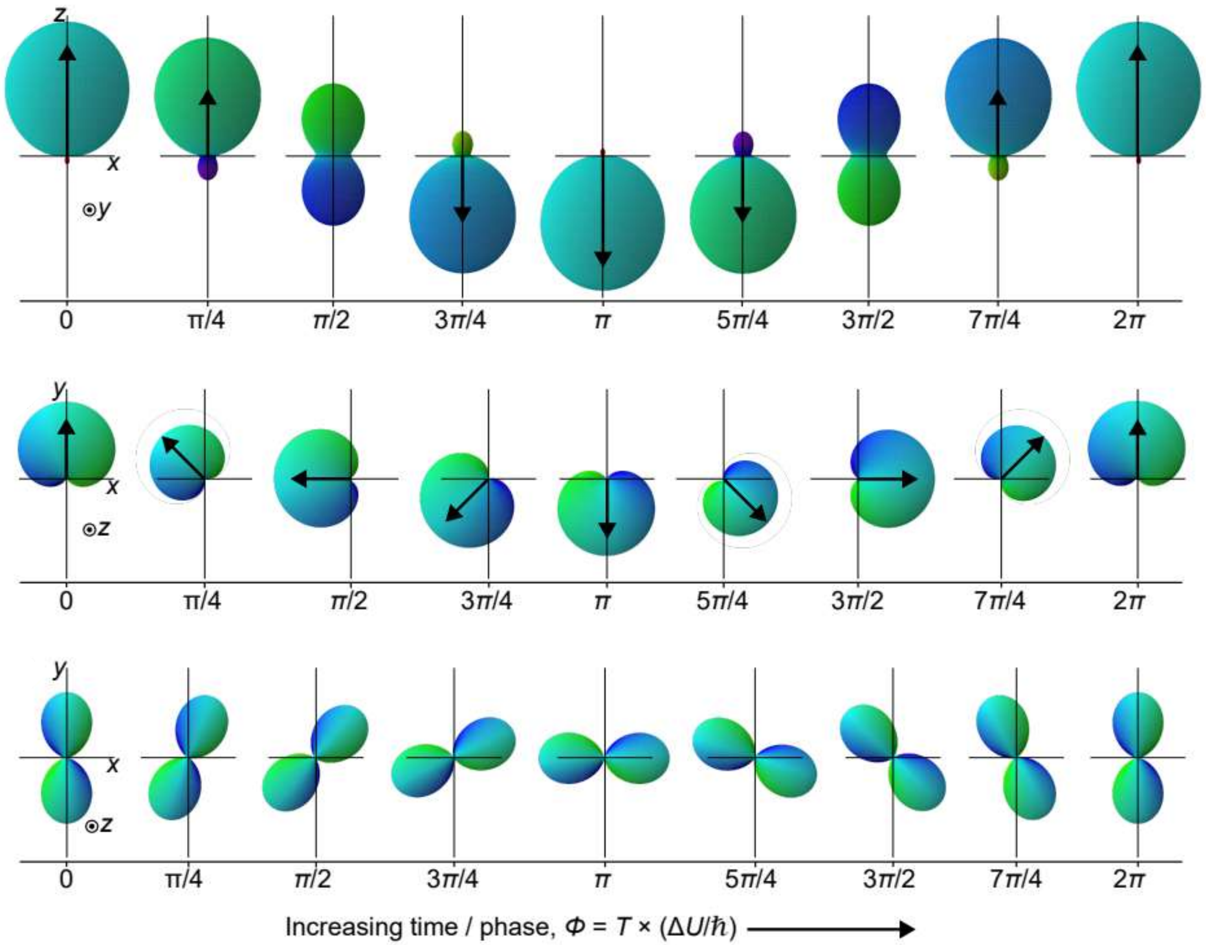
$\mu$ = reduced mass
$r$ = bond length

Critical E-field is $B_{rot}$ / d and gives a lab-frame dipole moment of d/3

1D = $3.34 \times 10^{-30}$ Cm
= 0.39343 $ea_0$

# Engineering oscillating dipoles

Use a microwave field to prepare a superposition of rotational states connected by an electric dipole transition




$$(|0,0\rangle + e^{-i\Phi}\,|1,0\rangle)/\sqrt{2}$$

$$(|0,0\rangle + e^{-i\Phi}\,|1,1\rangle)/\sqrt{2}$$

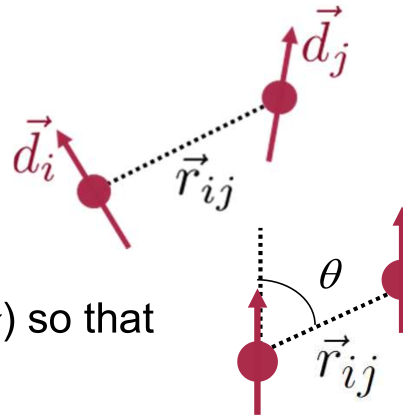
$$(|0,0\rangle + e^{-i\Phi}\,|2,2\rangle)/\sqrt{2}$$

$\Delta U$ is energy difference between states of the superposition

# Dipole-dipole interactions

The general form of the interaction between two dipoles is

$$H_{\mathrm{DDI}} = \frac{1}{4\pi\epsilon_0}\frac{\vec{d}_i\cdot\vec{d}_j - 3(\vec{d}_i\cdot\hat{e}_{ij})(\vec{d}_j\cdot\hat{e}_{ij})}{r_{ij}^3}$$




Usually, the dipoles are aligned to a quantisation axis (along $z$) so that

$$\hat{H}_{DDI}(R) = \frac{1}{4\pi\varepsilon_0 R^3}\Bigg[(1-3\cos^2\theta)\left(\hat{d}_i^0\hat{d}_j^0 + \frac{1}{2}\left(\hat{d}_i^+\hat{d}_j^- + \hat{d}_i^-\hat{d}_j^+\right)\right) - \frac{3}{\sqrt{2}}\sin\theta\cos\theta\left(e^{+i\phi}\left(\hat{d}_i^0\hat{d}_j^- + \hat{d}_i^-\hat{d}_j^0\right) - e^{-i\phi}\left(\hat{d}_i^0\hat{d}_j^+ + \hat{d}_i^+\hat{d}_j^0\right)\right) - \frac{3}{2}\sin^2\theta\left(e^{+2i\phi}\hat{d}_i^-\hat{d}_j^- + e^{-2i\phi}\hat{d}_i^+\hat{d}_j^+\right)\Bigg]$$

ΔM = 0

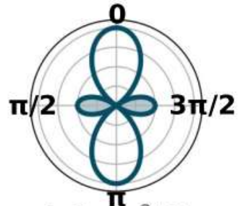
ΔM = ± 1

ΔM = ± 2

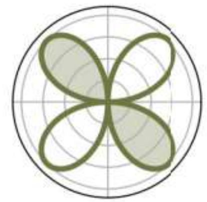
Here the dipole operators are $\hat{d}_0 = \hat{d}_z$ and $\hat{d}_{\pm 1} = \mp(\hat{d}_x \pm i\hat{d}_y)/\sqrt{2}$

For molecules, last two terms are generally suppressed as interaction energy << splitting between $M_N$ ($M_F$) levels

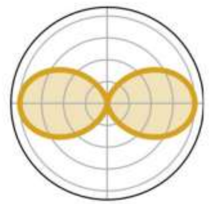
Interactions are **anisotropic** (positive when shaded)




∝1-3cos²(θ)



∝sin(θ)cos(θ)



∝sin²(θ)

Wadenpfuhl & Adams, PRA **111**, 062803 (2025)

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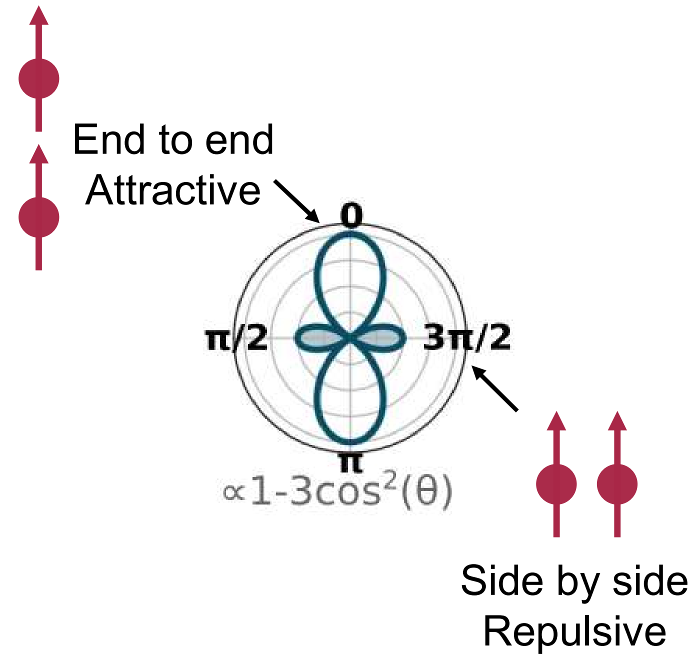
Usually, the dipoles are aligned to a quantisation axis (along $z$) so that

$$\hat{H}_{DDI}(R) = \frac{(1 - 3\cos^2\theta)}{4\pi\varepsilon_0 R^3}\left(\hat{d}_i^0 \hat{d}_j^0 + \frac{1}{2}\left(\hat{d}_i^+ \hat{d}_j^- + \hat{d}_i^- \hat{d}_j^+\right)\right)$$

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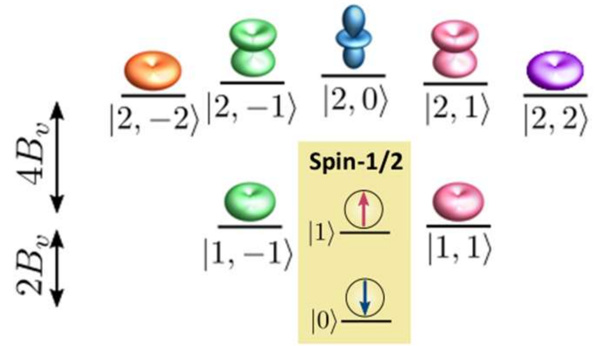
Wadenpfuhl & Adams, PRA **111**, 062803 (2025)

# Dipole-dipole interactions

Durham University

Let's now examine $H_{\mathrm{DDI}}$ in the two-state basis $|\downarrow\rangle = (0,0)$ and $|\uparrow\rangle = (1,0)$ so that

$$\hat{H}_{DDI}(R_{ij}) = \frac{(1 - 3\cos^2\theta)}{4\pi\varepsilon_0 R_{ij}^3}\hat{d}_i^0 \hat{d}_j^0$$




And we get an interaction matrix

$$\hat{H}_{ij} = \frac{1 - 3\cos^2\theta_{ij}}{|\mathbf{r}_i - \mathbf{r}_j|^3}\begin{pmatrix} d_\uparrow^2 & 0 & 0 & 0 \\ 0 & d_\downarrow d_\uparrow & d_{\downarrow\uparrow}^2 & 0 \\ 0 & d_{\downarrow\uparrow}^2 & d_\downarrow d_\uparrow & 0 \\ 0 & 0 & 0 & d_\downarrow^2 \end{pmatrix}$$

(resonant)
static dipoles
spin exchange

In the basis

$$\{|\uparrow_i\uparrow_j\rangle, |\uparrow_i\downarrow_j\rangle, |\downarrow_i\uparrow_j\rangle, |\downarrow_i\downarrow_j\rangle\}$$

Where
$$d_\downarrow = \langle\downarrow|\,\hat{d}_0\,|\downarrow\rangle$$
$$d_\uparrow = \langle\uparrow|\,\hat{d}_0\,|\uparrow\rangle$$
$$d_{\downarrow\uparrow} = \langle\downarrow|\,\hat{d}_0\,|\uparrow\rangle = \langle\uparrow|\,\hat{d}_0\,|\downarrow\rangle$$

See Wall, Hazzard, Rey arXiv:1406.4758 for details

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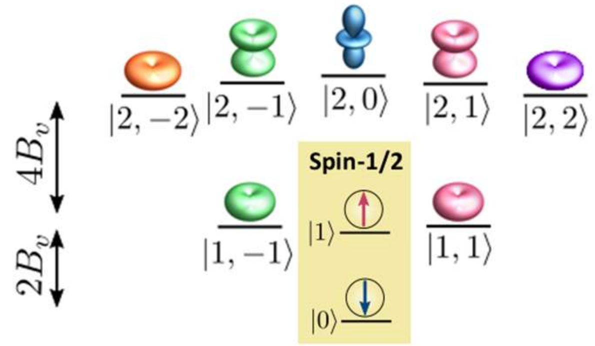


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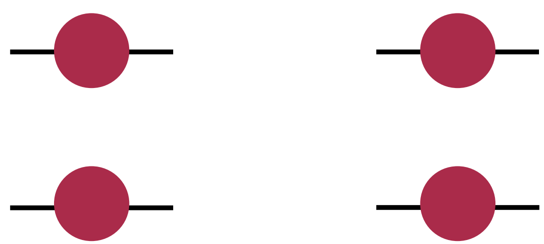
In the basis

$$\{|\uparrow_i\uparrow_j\rangle, |\uparrow_i\downarrow_j\rangle, |\downarrow_i\uparrow_j\rangle, |\downarrow_i\downarrow_j\rangle\}$$

(resonant) spin exchange

Where
$$d_\downarrow = \langle\downarrow|\hat{d}_0|\downarrow\rangle$$
$$d_\uparrow = \langle\uparrow|\hat{d}_0|\uparrow\rangle$$
$$d_{\downarrow\uparrow} = \langle\downarrow|\hat{d}_0|\uparrow\rangle = \langle\uparrow|\hat{d}_0|\downarrow\rangle$$



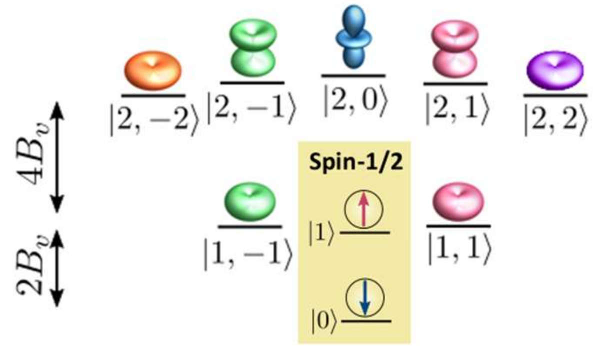
$|\uparrow\rangle = (1,0)$

$|\downarrow\rangle = (0,0)$

# Dipole-dipole interactions

Let's now examine $H_{\mathrm{DDI}}$ in the two-state basis $|\downarrow\rangle = (0,0)$ and $|\uparrow\rangle = (1,0)$ so that

$$\hat{H}_{DDI}(R_{ij}) = \frac{(1-3\cos^2\theta)}{4\pi\varepsilon_0 R_{ij}^3}\hat{d}_i^0\hat{d}_j^0$$




And we get an interaction matrix

$$\hat{H}_{ij} = \frac{1-3\cos^2\theta_{ij}}{|\mathbf{r}_i - \mathbf{r}_j|^3}\begin{pmatrix} d_\uparrow^2 & 0 & 0 & 0 \\ 0 & d_\downarrow d_\uparrow & d_{\downarrow\uparrow}^2 & 0 \\ 0 & d_{\downarrow\uparrow}^2 & d_\downarrow d_\uparrow & 0 \\ 0 & 0 & 0 & d_\downarrow^2 \end{pmatrix}$$

(resonant) spin exchange

In the basis

$$\{|\uparrow_i\uparrow_j\rangle, |\uparrow_i\downarrow_j\rangle, |\downarrow_i\uparrow_j\rangle, |\downarrow_i\downarrow_j\rangle\}$$

Where

$$d_\downarrow = \langle\downarrow|\,\hat{d}_0\,|\downarrow\rangle$$

$$d_\uparrow = \langle\uparrow|\,\hat{d}_0\,|\uparrow\rangle$$

$$d_{\downarrow\uparrow} = \langle\downarrow|\,\hat{d}_0\,|\uparrow\rangle = \langle\uparrow|\,\hat{d}_0\,|\downarrow\rangle$$

**These are all tunable!**

E.g. through applied electric field, choice of states or a magnetic field in the presence of hyperfine structure

# Dipole-dipole interactions

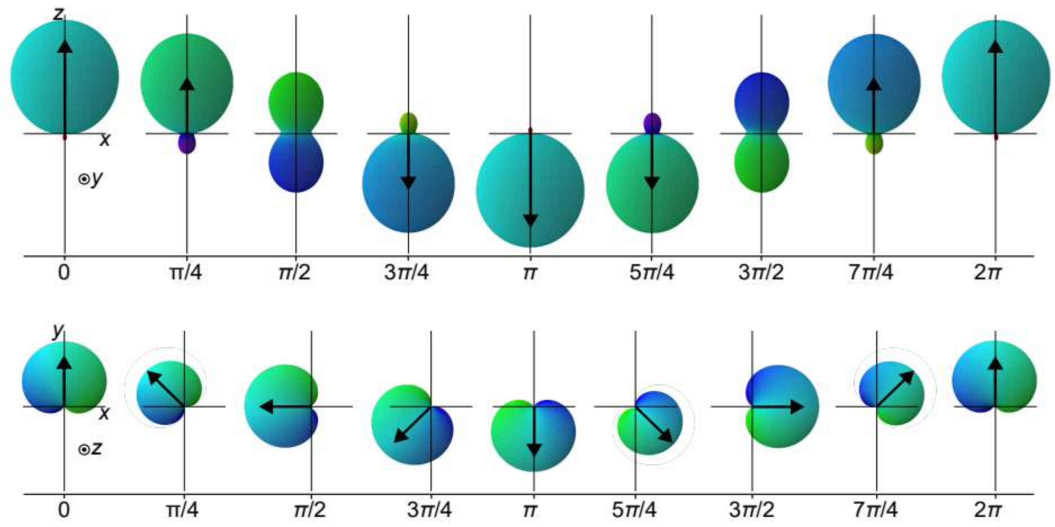
Transition dipole moments:

| $N \to N+1$ | $d_z(d_0)$ | $d_\pm(d_0)$ |
|---|---|---|
| 0 | $\frac{1}{\sqrt{3}}$ | $-\frac{1}{\sqrt{3}}$ |
| 1 | $\frac{2}{\sqrt{15}}$ | $-\sqrt{\frac{2}{5}}$ |
| 2 | $\frac{3}{\sqrt{35}}$ | $-\sqrt{\frac{3}{7}}$ |
| 3 | $\frac{4}{3\sqrt{7}}$ | $-\frac{2}{3}$ |
| 4 | $\frac{5}{3\sqrt{11}}$ | $-\sqrt{\frac{5}{11}}$ |
| 5 | $\frac{6}{\sqrt{143}}$ | $-\sqrt{\frac{6}{13}}$ |
| 6 | $\frac{7}{\sqrt{195}}$ | $-\sqrt{\frac{7}{15}}$ |
| 7 | $\frac{8}{\sqrt{255}}$ | $-2\sqrt{\frac{2}{17}}$ |
| 8 | $\frac{9}{\sqrt{323}}$ | $-\frac{3}{\sqrt{19}}$ |
| 9 | $\frac{10}{\sqrt{399}}$ | $-\sqrt{\frac{10}{21}}$ |
| 10 | $\frac{11}{\sqrt{483}}$ | $-\sqrt{\frac{11}{23}}$ |

Easy way to get ‘large’ interactions

Choice of states affects interactions:

$$(|0,0\rangle + \mathrm{e}^{-i\Phi}|1,0\rangle)/\sqrt{2}$$




$$(|0,0\rangle + \mathrm{e}^{-i\Phi}|1,1\rangle)/\sqrt{2}$$

“Dipolar”

$$V_{\mathrm{ddi}} = \frac{1 - 3\cos^2\Theta}{4\pi\epsilon_0 r^3} \times d_{\downarrow\uparrow}^2$$

Repulsive side to side (Θ=90°)

Attractive end to end (Θ=0°)

$$V_{\mathrm{ddi}} = \frac{3\cos^2\Theta - 1}{4\pi\epsilon_0 r^3} \times \frac{d_{\downarrow\uparrow}^2}{2}$$

Attractive side to side (Θ=90°)

Repulsive end to end (Θ=0°)

“Anti-dipolar”

# Comparing molecules



| Species | Dipole (D) | $2B_{rot}$ / h (GHz) | Critical E-field (V/cm) | Interaction at 1 μm (Hz) |
|---|---|---|---|---|
| NaLi | 0.463 | 22.8 | 48875 | 43 |
| LiK | 3.45 | 15.6 | 4488 | 2400 |
| LiRb | 4 | 13.2 | 3275 | 3200 |
| LiCs | 5.52 | 11.6 | 2086 | 6140 |
| NaK | 2.72 | 5.64 | 2058 | 1490 |
| NaRb | 3.1 | 4.18 | 1338 | 1940 |
| NaCs | 4.75 | 3.56 | 744 | 4540 |
| KRb | 0.574 | 2.23 | 3856 | 66 |
| KCs | 1.906 | 1.86 | 969 | 730 |
| RbCs | 1.2 | 0.98 | 811 | 290 |
| CaF | 3.07 | 10.27 | 3320 | 1900 |

Critical E-field is $B_{rot}$ / d and gives a lab-frame dipole moment of d/3
Interaction assumes transition dipole of d/sqrt(3) and maximum angular factor

1D = $3.34 \times 10^{-30}$ Cm
= 0.39343 $ea_0$

# Dipole-dipole interactions

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The Hamiltonian can be re-written in terms of spin operators

$$\hat{S}_z^{(i)} = \frac{1}{2}\left(\left|\uparrow^{(i)}\right\rangle\left\langle\uparrow^{(i)}\right| - \left|\downarrow^{(i)}\right\rangle\left\langle\downarrow^{(i)}\right|\right) \qquad \hat{S}_+^{(i)} = \left|\uparrow^{(i)}\right\rangle\left\langle\downarrow^{(i)}\right| \qquad \hat{S}_-^{(i)} = \left|\downarrow^{(i)}\right\rangle\left\langle\uparrow^{(i)}\right|$$

$$\hat{H}_{\mathrm{dd}}^{q=0} = \frac{1-3\cos^2\Theta}{4\pi\epsilon_0 r^3} \times \left(\frac{J_\perp}{2}\left(\hat{S}_+^{(i)}\hat{S}_-^{(j)} + \hat{S}_-^{(i)}\hat{S}_+^{(j)}\right) + J_z \hat{S}_z^{(i)}\hat{S}_z^{(j)}\right)$$

XXZ Hamiltonian

Or equivalently as

$$\hat{H}_{\mathrm{dd}}^{q=0} = \frac{1-3\cos^2\Theta}{4\pi\epsilon_0 r^3} \times \left(J_\perp\left(\hat{S}_x^{(i)}\hat{S}_x^{(j)} + \hat{S}_y^{(i)}\hat{S}_y^{(j)}\right) + J_z \hat{S}_z^{(i)}\hat{S}_z^{(j)}\right)$$

Here $J_\perp = 2d_{\uparrow\downarrow}^2$ and $J_z = (d_\uparrow - d_\downarrow)^2$

See Wall, Hazzard, Rey arXiv:1406.4758 for details

# Dipole-dipole interactions

Applying this to an array of molecules in a (partially filled) lattice we get

$$H = \frac{1}{2}\sum_{i \neq j} V_{\mathrm{dd}} \left[ J_z S_i^z S_j^z + \frac{J_\perp}{2}(S_i^+ S_j^- + S_i^- S_j^+) + W(S_i^z n_j + n_i S_j^z) + V n_i n_j \right]$$

Here the $W$ term is a spin-density interaction where a molecule at one site creates an effective magnetic field along $z$ for a spin on another site, and the $V$ term describes density-density interactions.

Where $W = (d_\uparrow^2 - d_\downarrow^2)/2$ and $V = (d_\uparrow + d_\downarrow)^2/4$

Reduce the lattice depth to introduce tunnelling and you get the $t$-$J$-$V$-$W$ model

$m$ = two molecular states

$$H = -t \sum_{\langle i,j \rangle m} [c_{im}^\dagger c_{jm} + \mathrm{H.c.}] + \sum_{i \neq j} |\mathbf{R}_i - \mathbf{R}_j|^{-3} \times \left[ \frac{J_\perp}{2} S_i^+ S_j^- + \frac{J_z}{2} S_i^z S_j^z + \frac{V}{2} n_i n_j + W n_i S_j^z \right]$$

Note this is a natural description of molecules in a lattice!

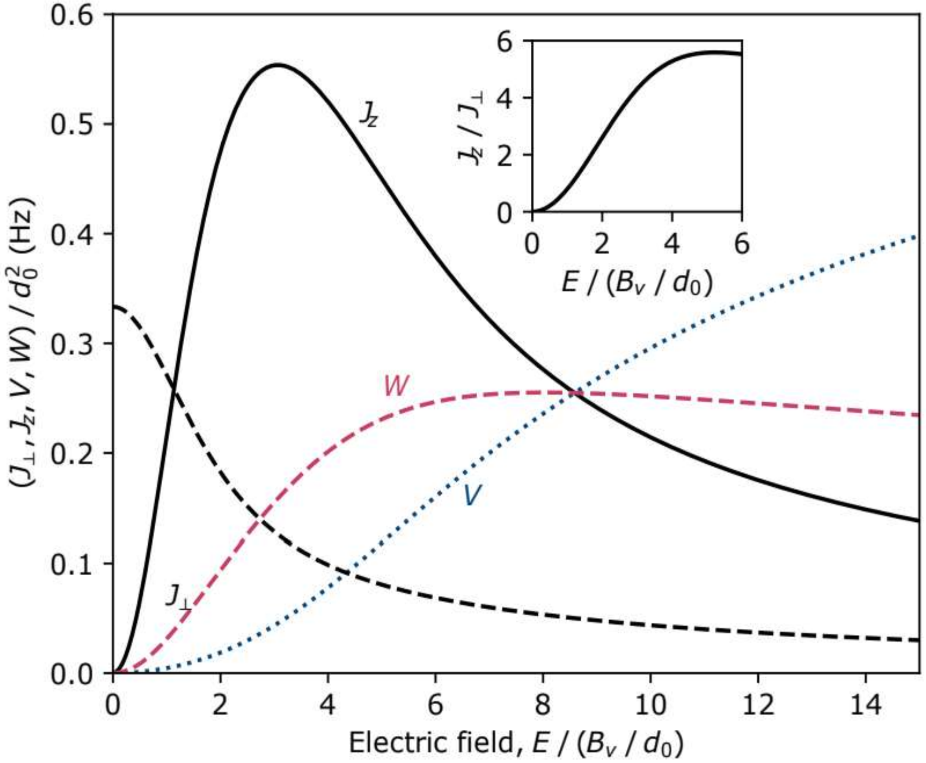
(note that $t$-$J$ models are believed to underlie certain high-temperature superconductors)

Gorshkov *et al*., Phys. Rev. Lett. **107**, 115301 (2011)

# Tunability of the model



Model parameters tune with electric field

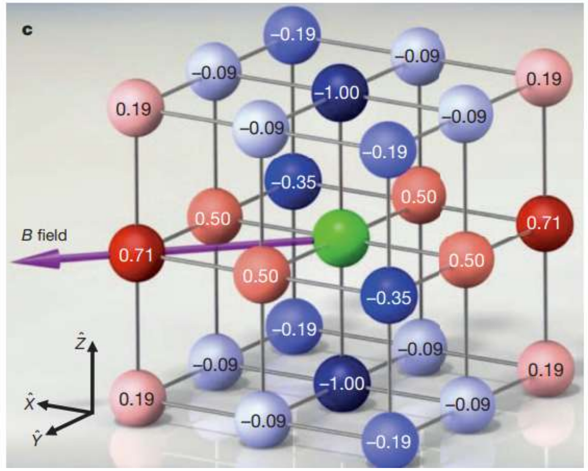



Special cases:

- → XX Hamiltonian (no electric field)
- → Ising Hamiltonian (no transition dipole)
- → Heisenberg Hamiltonian ($J_z = J_\perp$)

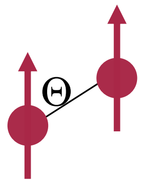
And geometry (DDI is anisotropic)

E.g. relative strength of spin-exchange in a lattice

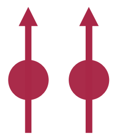



Nature **501**, 521-525 (2013)

Using (0,0) & (1,1)




$$V_{\mathrm{ddi}} = \frac{3\cos^2\Theta - 1}{4\pi\epsilon_0 r^3} \times \frac{d_{\downarrow\uparrow}^2}{2}$$



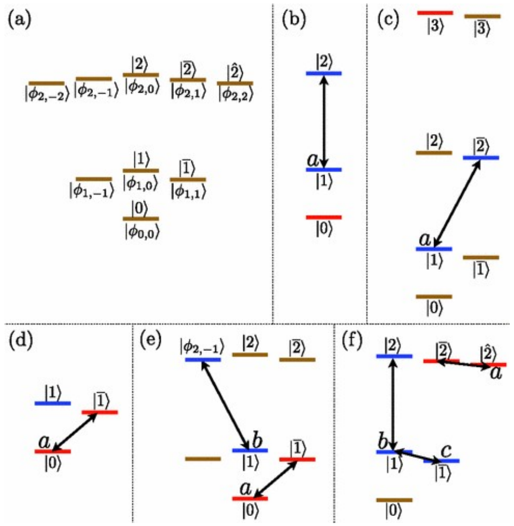
Attractive

Repulsive

# Tunability of the model!

They also tune with choice of states…

"Quantum magnetism with polar alkali-metal dimers"
Gorshkov *et al.*, Phys. Rev. A **84**, 033619 (2011)




Highly tunable generalisation of the *t*-*J* model: the *t*-*J*-*V*-*W* model

| | Rotor states used | Expressions for $V, W, J_z, J_\perp$<br>$V = [(A_0+A_1)^2 + B_0 + B_1]/4$<br>$W = [A_0^2 + B_0 - A_1^2 - B_1]/2$<br>$J_z = (A_0 - A_1)^2 + B_0 + B_1$ | Special features |
| --- | --- | --- | --- |
| No. 1 | $\lvert m_0\rangle = \lvert 0\rangle$<br>$\lvert m_1\rangle = \lvert 1\rangle$<br>Fig. 3(a) | $V = (\mu_0+\mu_1)^2/4$<br>$W = (\mu_0^2 - \mu_1^2)/2$<br>$J_z = (\mu_0 - \mu_1)^2$<br>$J_\perp = 2\mu_{01}^2$ | Simplest<br>At small $dE/B$, $V \approx W \approx J_z \approx 0$ and $J_\perp > 0$, yielding the dipolar $t$-$J_\perp$ Hamiltonian [7] |
| No. 2 | $\lvert m_0\rangle = \lvert 1\rangle$<br>$\lvert m_1\rangle = \lvert 3\rangle$<br>Fig. 3(a) | $V = (\mu_1+\mu_3)^2/4$<br>$W = (\mu_1^2 - \mu_3^2)/2$<br>$J_z = (\mu_1 - \mu_3)^2$<br>$J_\perp = 2\mu_{13}^2$ | At small $dE/B$, $\mu_1\mu_3 > \mu_{13}^2$, which may help stabilize the system against chemical reactions (see Sec. VI) |
| No. 3 | $\lvert m_0\rangle = \lvert 0\rangle$<br>$\lvert m_1\rangle = \lvert \bar{1}\rangle$<br>Fig. 3(a) | $V = (\mu_0+\mu_{\bar{1}})^2/4$<br>$W = (\mu_0^2 - \mu_{\bar{1}}^2)/2$<br>$J_z = (\mu_0 - \mu_{\bar{1}})^2$<br>$J_\perp = -\mu_{0\bar{1}}^2$ | Simplest configuration with $J_\perp < 0$<br>A microwave field is required to shift $\lvert\phi_{1,-1}\rangle$ out of resonance with $\lvert\bar{1}\rangle$ |
| No. 4 | $\lvert m_0\rangle = \lvert 0\rangle$<br>$\lvert m_1\rangle = \sqrt{a}\lvert 1\rangle + \sqrt{1-a}\lvert 2\rangle$<br>Fig. 3(b) | $A_0 = \mu_0$<br>$A_1 = a\mu_1 + (1-a)\mu_2$<br>$B_0 = 0$<br>$B_1 = 2\mu_{12}^2 a(1-a)$<br>$J_\perp = 2(\mu_{01}^2 a + \mu_{02}^2(1-a))$ | At $(dE/B,a) = (1.25,0.74)$, $W = 0$, $J_z = J_\perp = 0.36d^2$, and $V = 0.1J_z$, making Eq. (5) similar to the SU(2)-symmetric $t$-$J$-$V$ model, which exhibits suppressed phase separation [60] |
| No. 5 | $\lvert m_0\rangle = \sqrt{a}\lvert 0\rangle + \sqrt{1-a}\lvert \bar{1}\rangle$<br>$\lvert m_1\rangle = \lvert 1\rangle$<br>Fig. 3(d) | $A_0 = a\mu_0 + (1-a)\mu_{\bar{1}}$<br>$A_1 = \mu_1$<br>$B_0 = -\mu_{0\bar{1}}^2 a(1-a)$<br>$B_1 = 0$<br>$J_\perp = 2a\mu_{01}^2 - (1-a)\mu_{1\bar{1}}^2$ | $J_\perp = 0$ can be achieved at any $dE/B$ by adjusting $a$<br>$J_z < 0$ can be achieved<br>$V < 0$ can be achieved |
| No. 6 | $\lvert m_0\rangle = \lvert 3\rangle$<br>$\lvert m_1\rangle = \sqrt{a}\lvert 1\rangle + \sqrt{1-a}\lvert \bar{2}\rangle$<br>Fig. 3(c) | $A_0 = \mu_3$<br>$A_1 = a\mu_1 + (1-a)\mu_{\bar{2}}$<br>$B_0 = 0$<br>$B_1 = -a(1-a)\mu_{1\bar{2}}$<br>$J_\perp = 2a\mu_{13}^2 - (1-a)\mu_{3\bar{2}}^2$ | $J_z = 0$ and $J_\perp = 0$ lines intersect in $(dE/B,a)$ space at $(dE/B,a) = (2.6,0.92)$; so if we write $J_z = \lvert J\rvert\cos\psi$ and $J_\perp = \lvert J\rvert\sin\psi$, arbitrary $\psi$ can be achieved around that point |
| No. 7 | $\lvert m_0\rangle = a\lvert 0\rangle + \sqrt{1-a}\lvert \bar{1}\rangle$<br>$\lvert m_1\rangle = b\lvert 1\rangle + \sqrt{1-b}\lvert\phi_{2,-1}\rangle$<br>Fig. 3(e) | $A_0 = a\mu_0 + (1-a)\mu_{\bar{1}}$<br>$A_1 = b\mu_1 + (1-b)\mu_{\bar{2}}$<br>$B_0 = -a(1-a)\mu_{0\bar{1}}^2$<br>$B_1 = -b(1-b)\mu_{1\bar{2}}^2$<br>$J_\perp = 2ab\mu_{01}^2 - a(1-b)\mu_{0\bar{2}}^2$<br>$-(1-a)b\mu_{\bar{1}1}^2$ | At $(dE/B,a,b) = (1.7,0.33,0.81)$, $W = 0$ and $J_z = J_\perp = -4V = 0.089d^2$, making Eq. (5) very similar to the standard $t$-$J$ model [8] |
| No. 8 | $\lvert m_0\rangle = \sqrt{a}\lvert \hat{2}\rangle + \sqrt{1-a}\lvert \bar{2}\rangle$<br>$\lvert m_1\rangle = \sqrt{b}\lvert 1\rangle + \sqrt{c}\lvert \bar{1}\rangle$<br>$+\sqrt{1-b-c}\lvert 2\rangle$<br>Fig. 3(f) | $A_0 = a\mu_{\hat{2}} + (1-a)\mu_{\bar{2}}$<br>$A_1 = b\mu_1 + c\mu_{\bar{1}} + (1-b-c)\mu_2$<br>$B_0 = -a(1-a)\mu_{\hat{2}\bar{2}}^2$<br>$B_1 = -bc\mu_{1\bar{1}}^2 - c(1-b-c)\mu_{2\bar{1}}^2$<br>$+2b(1-b-c)\mu_{12}^2$<br>$J_\perp = 2(1-a)c\mu_{\bar{2}\bar{1}}^2 - (1-a)b\mu_{\bar{2}1}^2$<br>$-(1-a)(1-b-c)\mu_{\bar{2}2}^2 - ac\mu_{\hat{2}\bar{1}}^2$ | The manifolds $V = 0$, $W = 0$, $J_z = 0$, and $J_\perp = 0$ intersect in $(dE/B,a,b,c)$ space at $(dE/B,a,b,c) = (2.97,0.059,0.56,0.38)$; full control over $V$, $W$, $J_z$, and $J_\perp$ is achievable around that point |

# Summary: an incredibly rich quantum system

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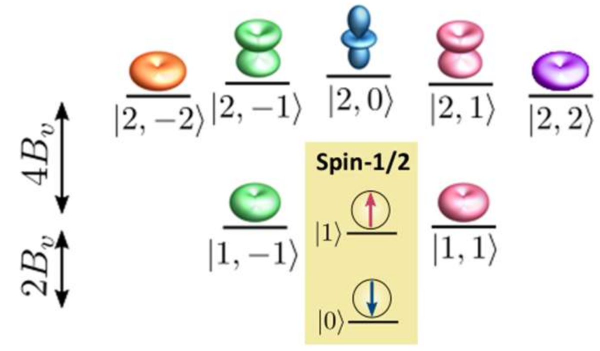
Even for the simplest case of two states and pinned molecules…




## Quantum magnetism: XXZ Hamiltonian

$$H_{\mathrm{XXZ}} = \sum_{i \neq j} \left[ \frac{J_\perp}{2} (S_i^+ S_j^- + S_i^- S_j^+) + J_z S_i^z S_j^z \right]$$

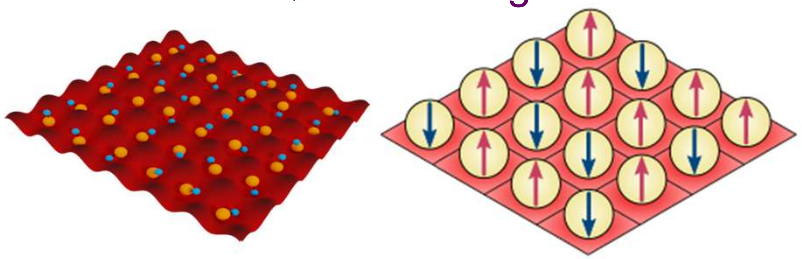
$J_\perp \propto |\langle \uparrow | d_0 | \downarrow \rangle|^2$

Spin exchange

$J_z \propto (\langle \uparrow | d_0 | \uparrow \rangle - \langle \downarrow | d_0 | \downarrow \rangle)^2$

"Ising" interaction

Simulate Quantum Magnetism

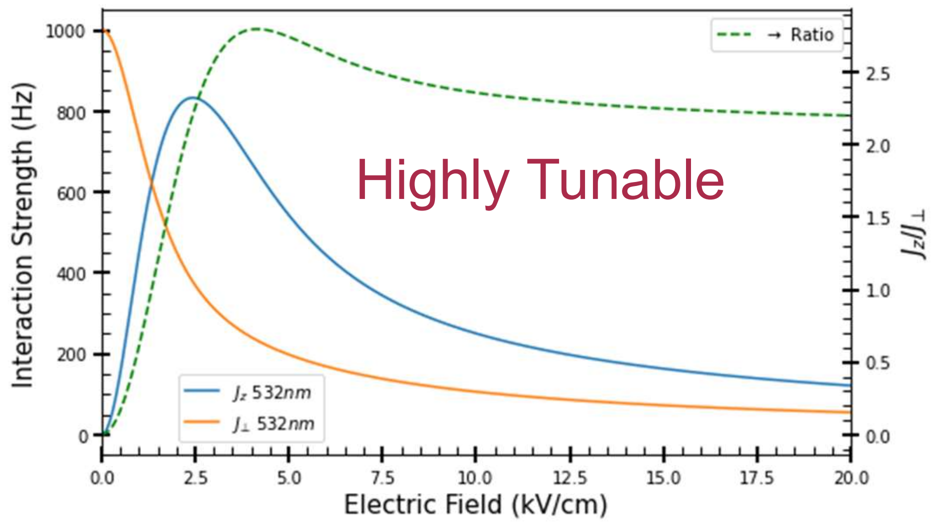


Special cases:

→ XX Hamiltonian (no electric field)

→ Ising Hamiltonian (no transition dipole)

→ Heisenberg Hamiltonian




= RbCs

$d_0$ ~ 1.2 D

**Becomes even richer with more states and tunnelling in the lattice!**

Questions?

But how do we make an array of ultracold polar molecules?

# The inspiration

Durham University

VOLUME 90, NUMBER 11 PHYSICAL REVIEW LETTERS week ending 21 MARCH 2003

## Creation of a Dipolar Superfluid in Optical Lattices

B. Damski,[1,2] L. Santos,[1] E. Tiemann,[3] M. Lewenstein,[1] S. Kotochigova,[4] P. Julienne,[4] and P. Zoller[5]

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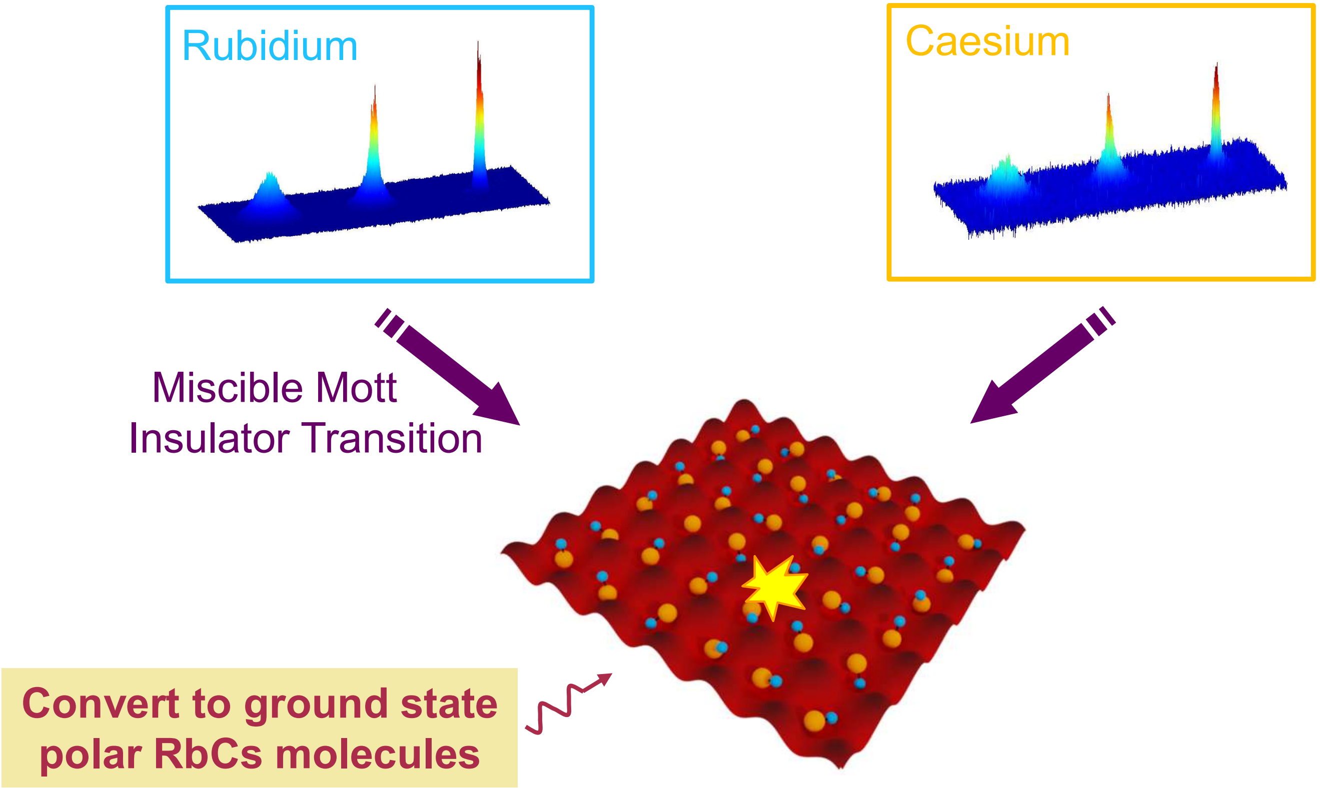
[2]*Instytut Fizyki, Uniwersytet Jagielloński, Reymonta 4, PL-30 059 Kraków, Poland*
[3]*Institut für Quantenoptik, Universität Hannover, D-30167 Hannover, Germany*
[4]*National Institute of Standards and Technology, Gaithersburg, Maryland 20899*
[5]*Institut für Theoretische Physik, Universität Innsbruck, A-6020 Innsbruck, Austria*

(Received 20 August 2002; published 17 March 2003)

We show that, by loading a Bose-Einstein condensate of two different atomic species into an optical lattice, it is possible to achieve a Mott-insulator phase with exactly one atom of each species per lattice site. A subsequent photoassociation leads to the formation of one heteronuclear molecule with a large electric dipole moment, at each lattice site. The melting of such a dipolar Mott insulator creates a dipolar superfluid, and eventually a dipolar molecular condensate.

# Making an array of polar molecules




Jaksch *et al.*, PRL **89**, 040402 (2002)
Damski *et al.,* PRL **90**, 110401 (2003)

# Producing molecules using association

1. Create a high phase space density atomic mixture.

3. Transfer to the rovibrational ground state using stimulated Raman adiabatic passage (STIRAP).

**$Cs_2$** : Danzl *et al.*, Science **321**, 5892 (2008)

**$Rb_2$** : Lang *et al.*, PRL **101**, 133005 (2008)

**KRb** : Ni *et al.*, Science **322**, 5899 (2008)

# The world of bialkali molecules

Durham University


KRb – JILA (Ye)
RbCs – Innsbruck (Nägerl)
KRb – Tokyo (Inouye)
RbCs – Durham (Cornish)

NaK – MIT (Zwierlein)
NaRb – Hong-Kong (Wang)
NaLi – MIT (Ketterle) [Triplet]
NaK – MPQ (Luo/Bloch)

NaK – Hefei (Pan)
KRb – Harvard (Ni)
NaK – Hannover (Ospelkaus)
NaCs – Harvard (Ni)

NaRb – Princeton (Bakr)
NaCs – Columbia (Will)

# Aside: direct laser cooling

No selection rule on vibration
FCF – square of overlap integral

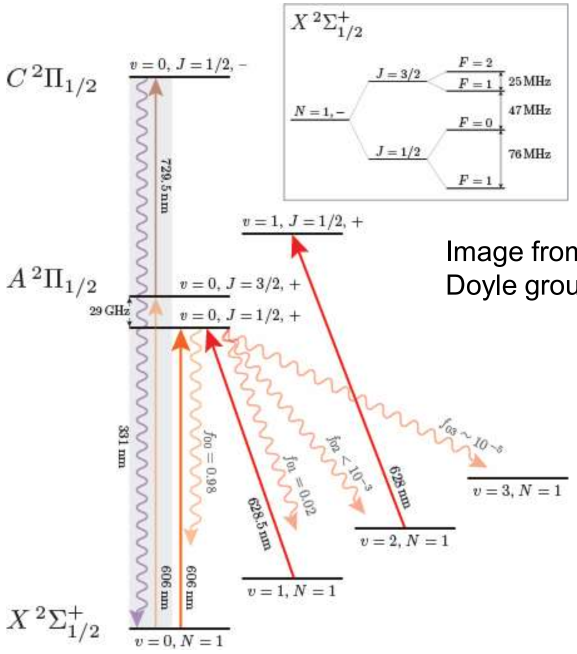
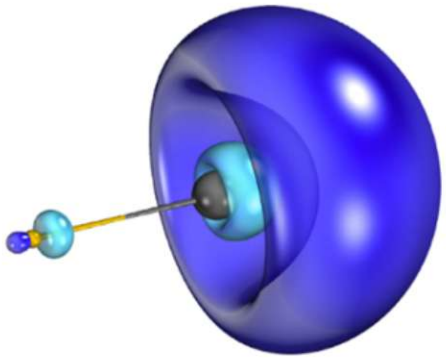



Image from
Doyle group

However, some molecules have highly diagonal FCFs: SrF, CaF, YO, CaOH…

These are all molecules where the valence electron does not participate in the bond…

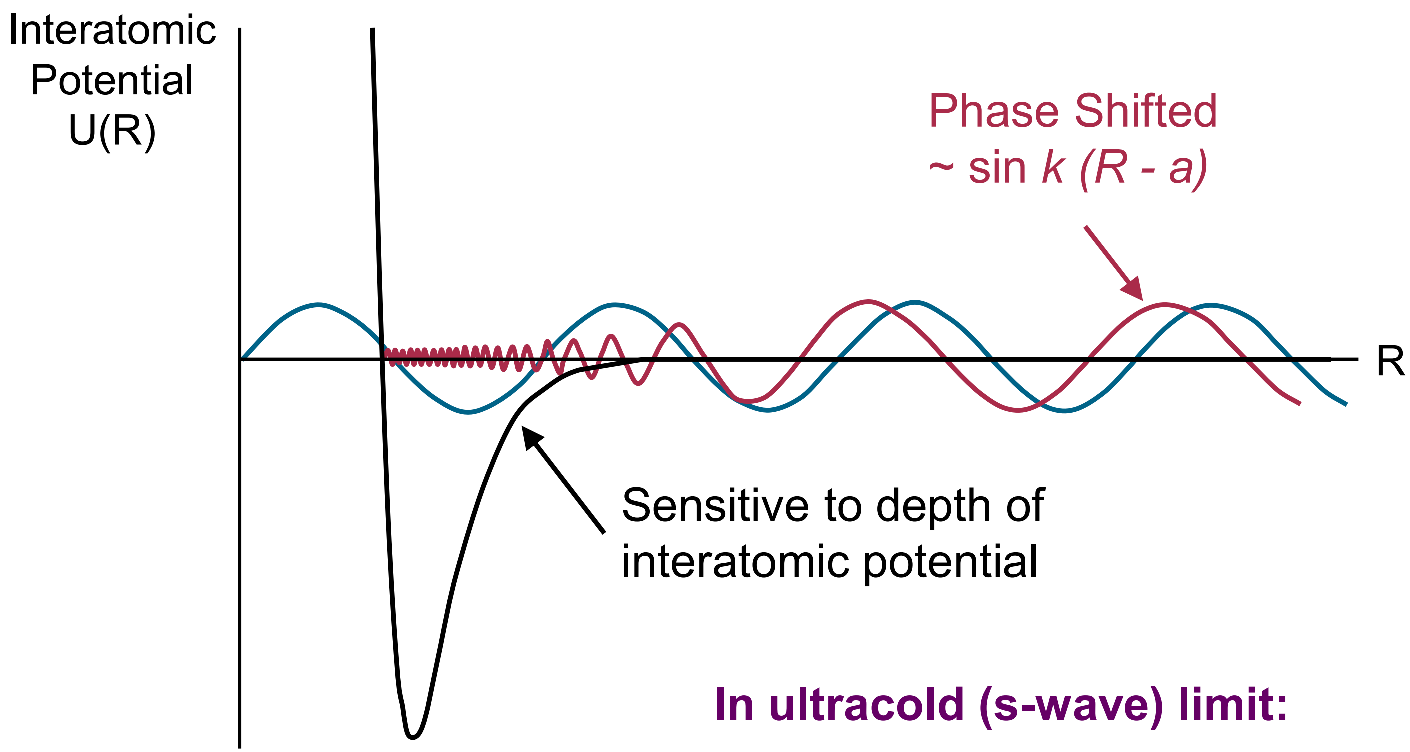


From Nature Physics **20**, 702–712 (2024)

The calculated valence electron distribution
for the ground state of CaF molecules.
Behaves similarly to an alkali atom, with transitions of the single valence electron largely independent from molecular vibrations

# Assembling molecules
# Feshbach resonances
# Magnetoassociation
# and STIRAP

# What is a scattering length?



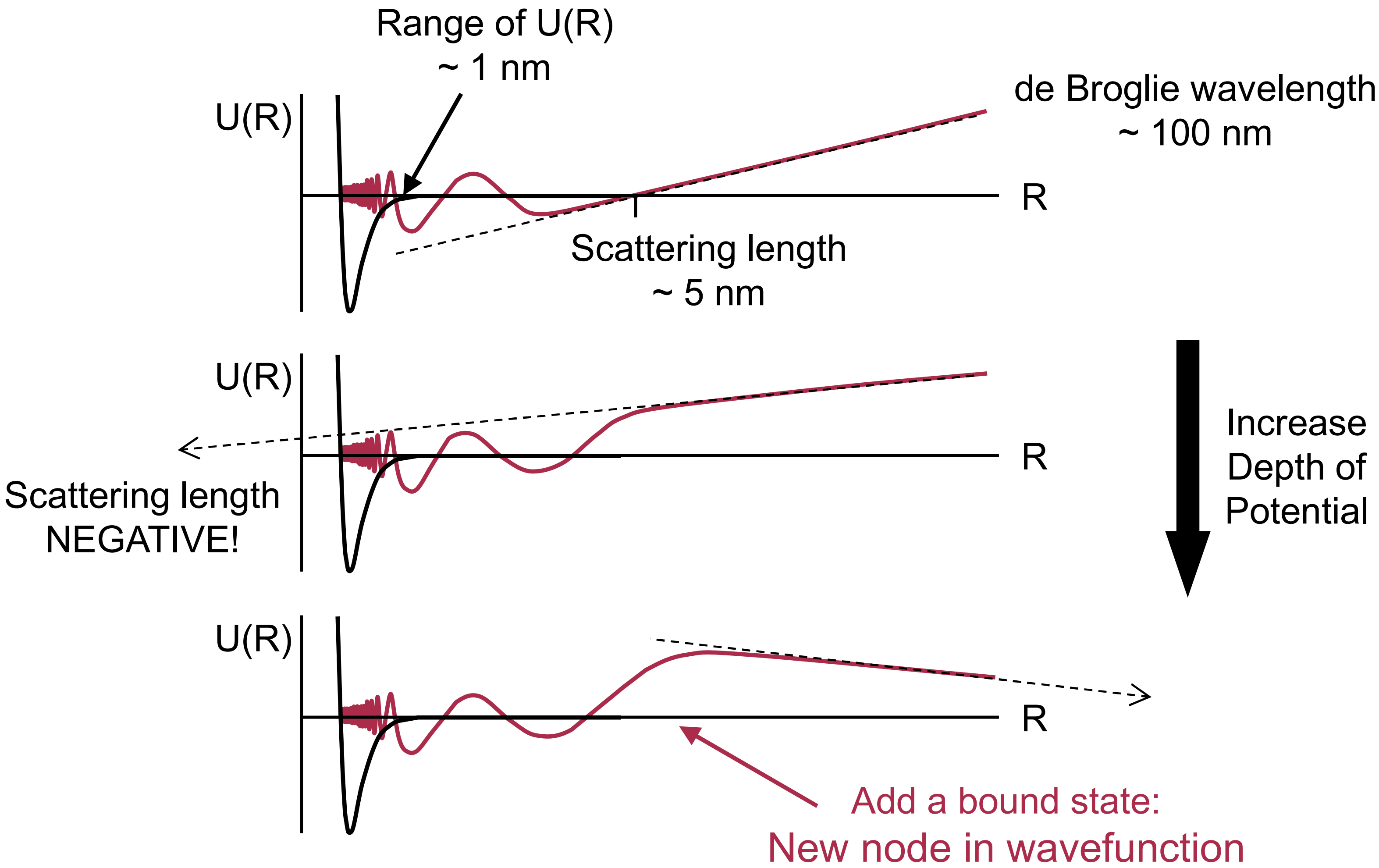

**In ultracold (s-wave) limit:**

**Scattering length ≡ radius of "hard sphere"**

**Elastic cross section = $8\pi a^2$**

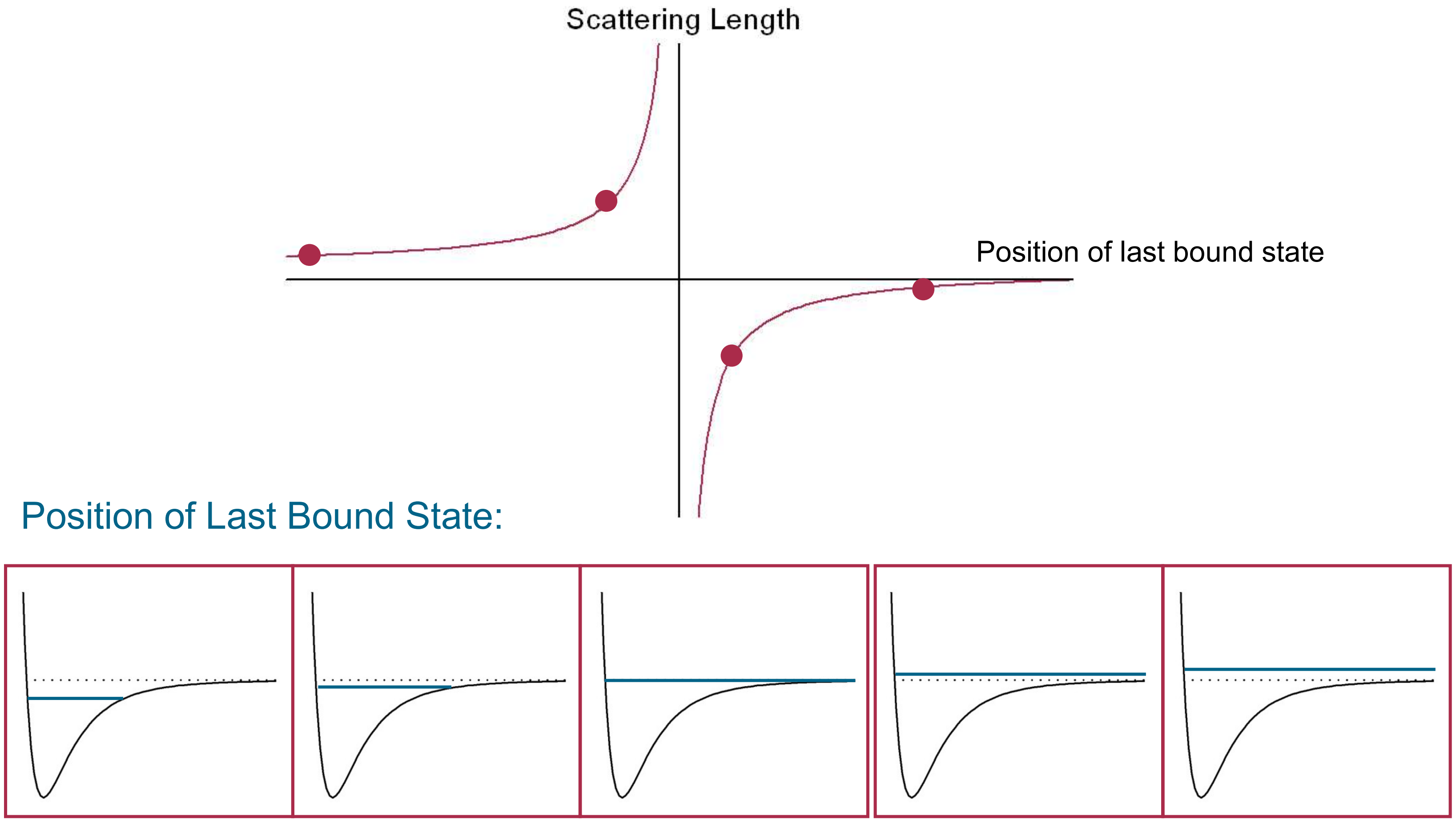
[Also see Chin *et al*., Rev. Mod. Phys. 82, 1225-1286 (2010)]

# A more accurate picture




[Also see Chin *et al*., Rev. Mod. Phys. 82, 1225-1286 (2010)]

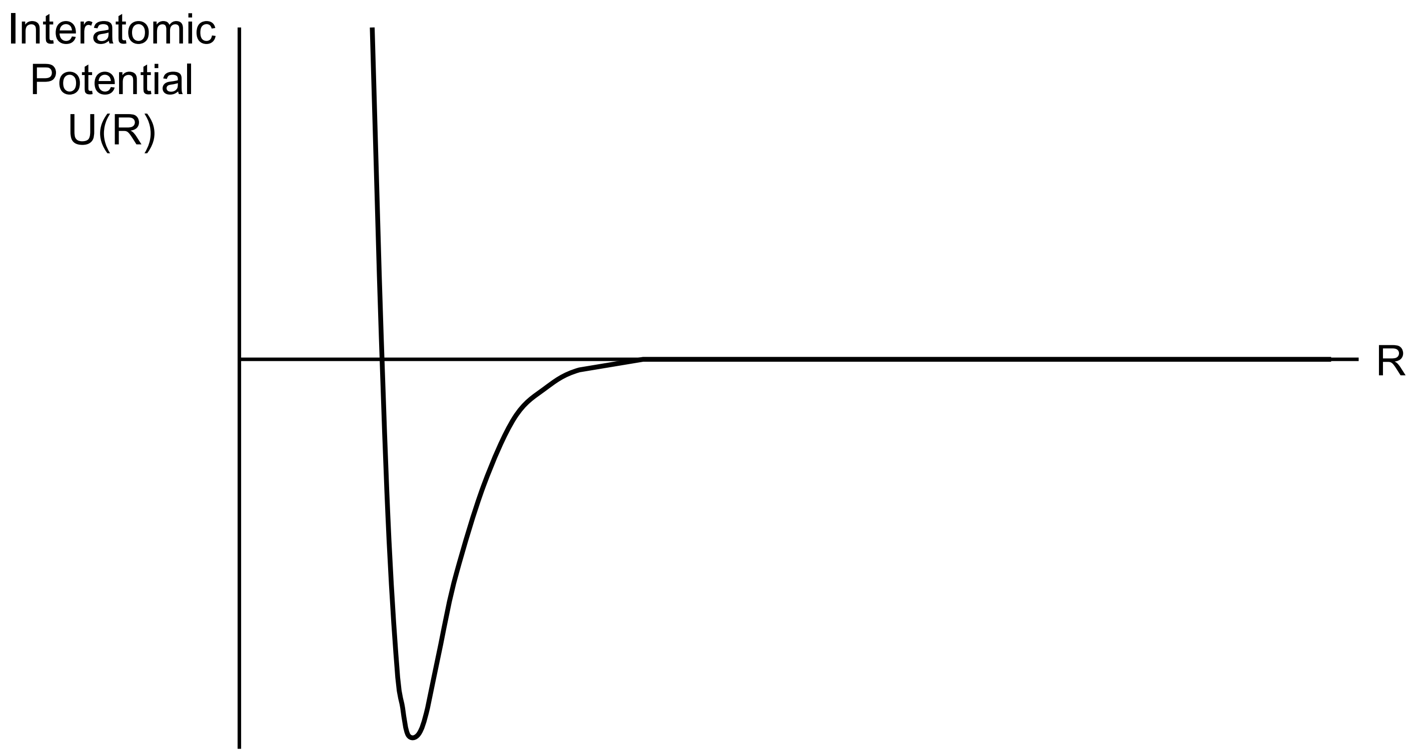
# Scattering length & bound states




[Also see Chin *et al.*, Rev. Mod. Phys. 82, 1225-1286 (2010)]

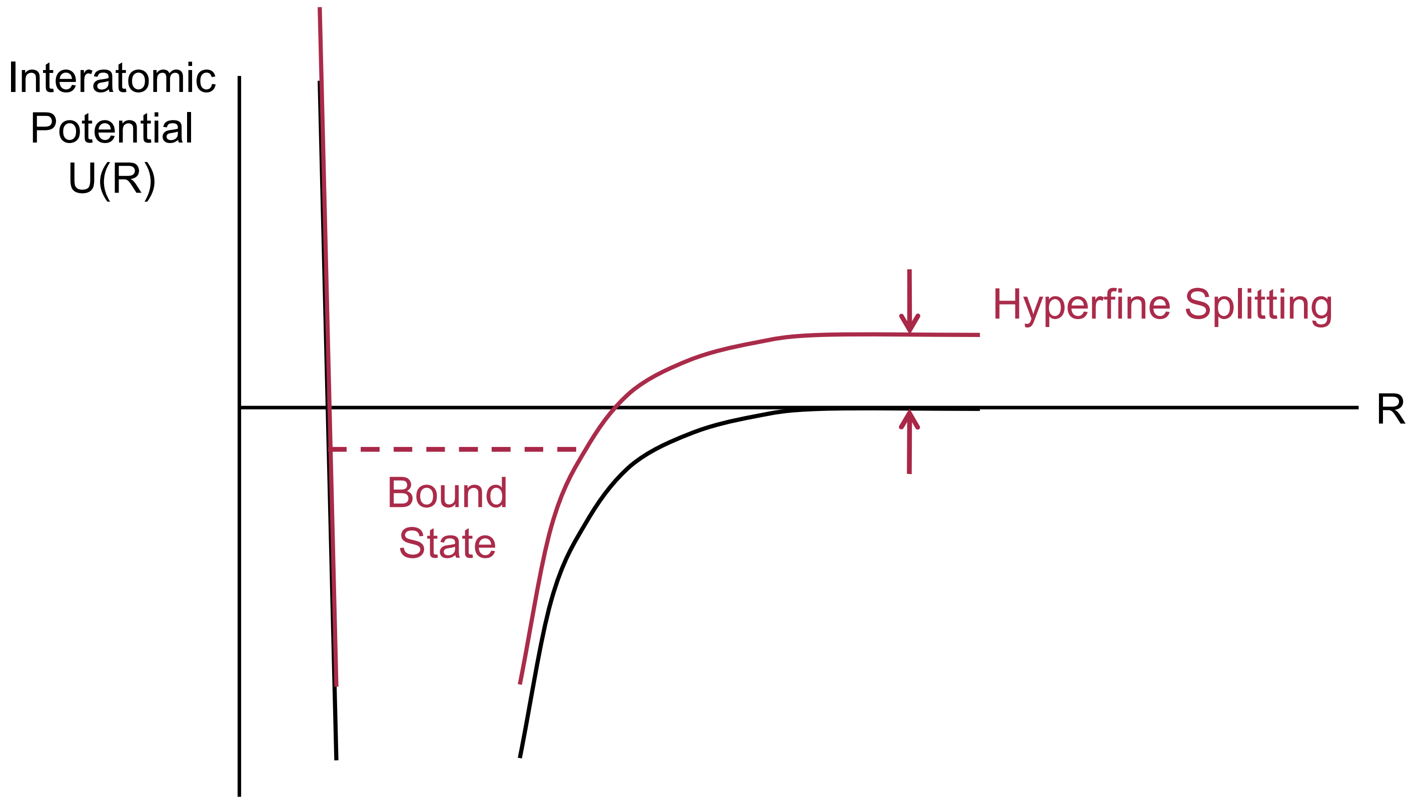
# How do we move the bound state?





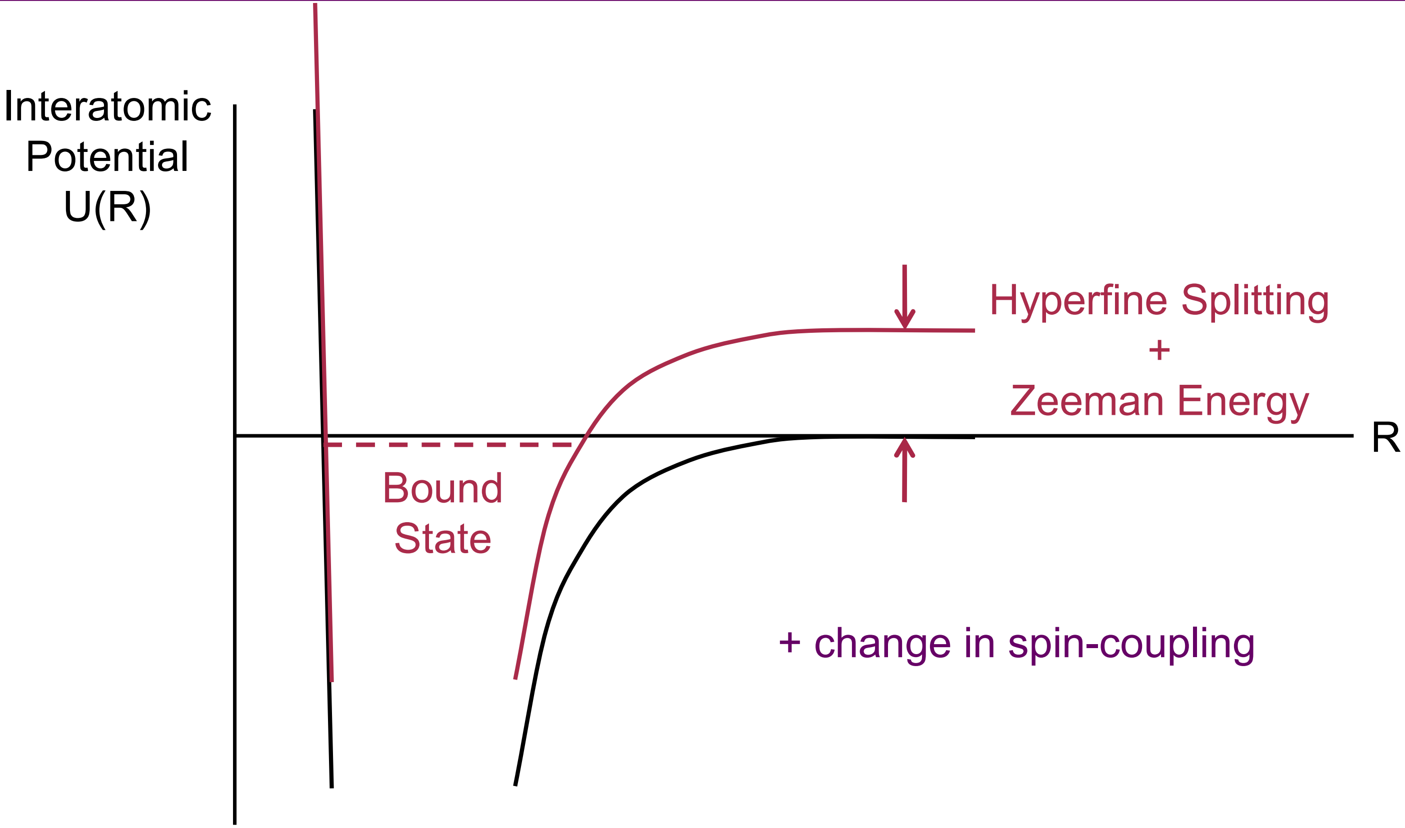

[Also see Chin *et al.*, Rev. Mod. Phys. 82, 1225-1286 (2010)]

# How do we move the bound state?



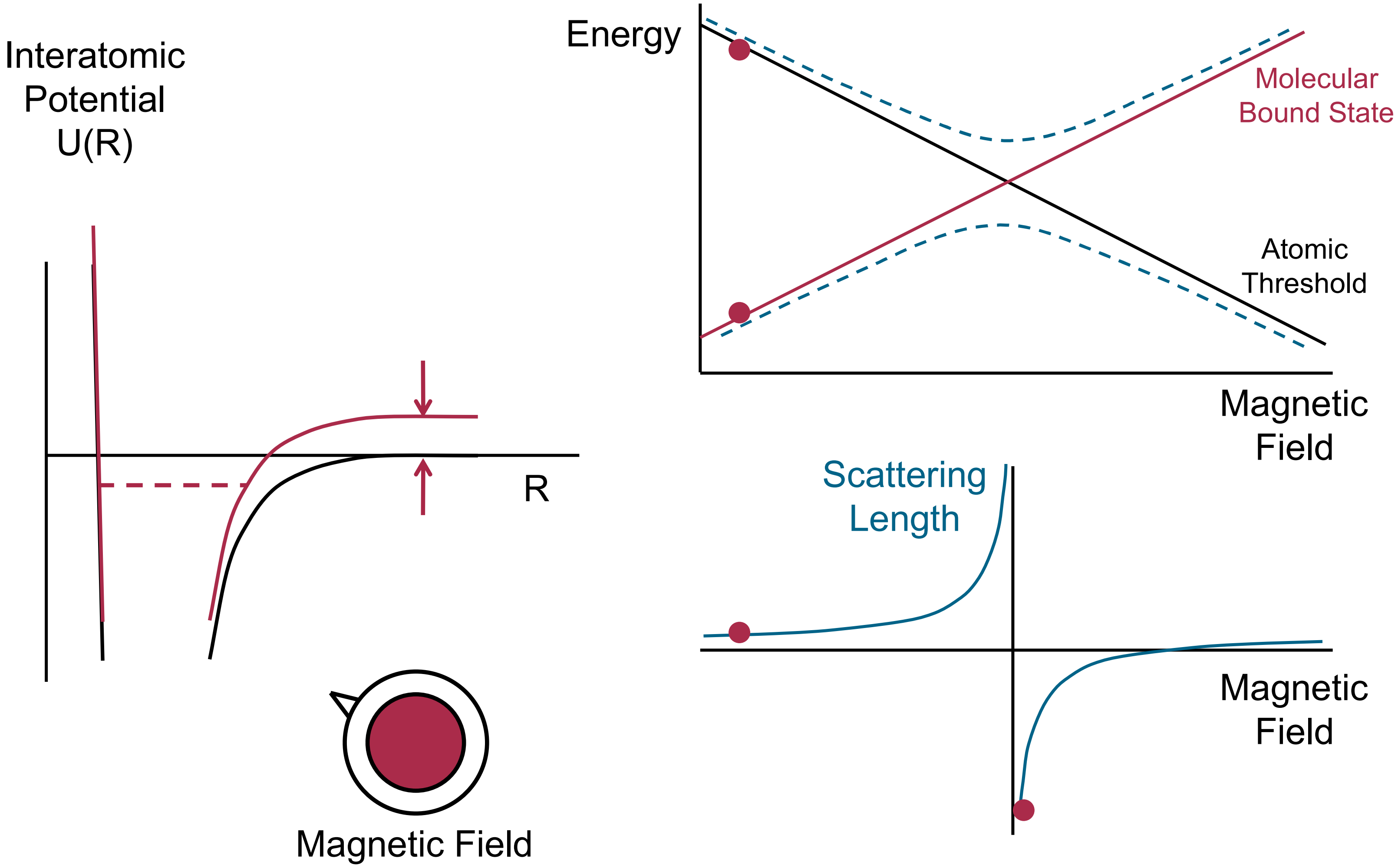

[Also see Chin *et al.*, Rev. Mod. Phys. 82, 1225-1286 (2010)]

# How do we move the bound state?

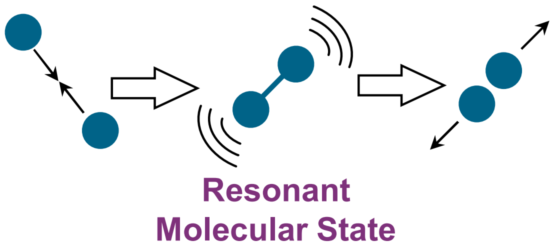


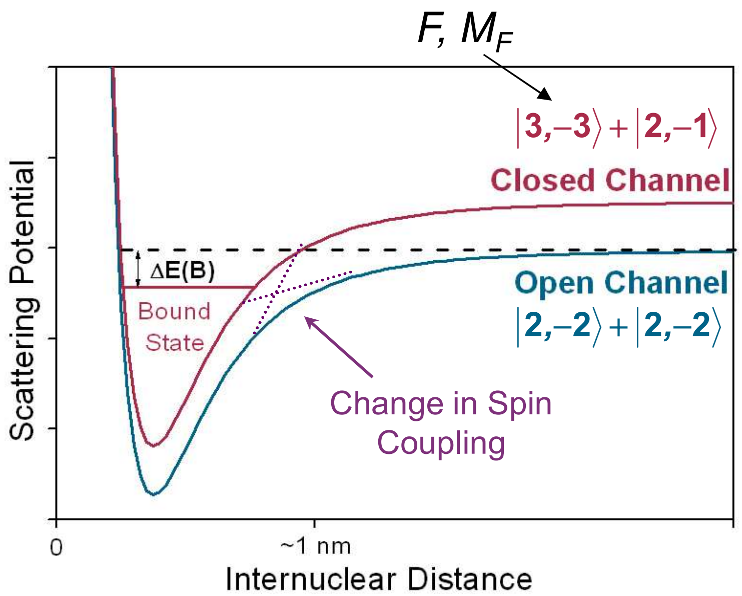

[Also see Chin *et al.*, Rev. Mod. Phys. 82, 1225-1286 (2010)]

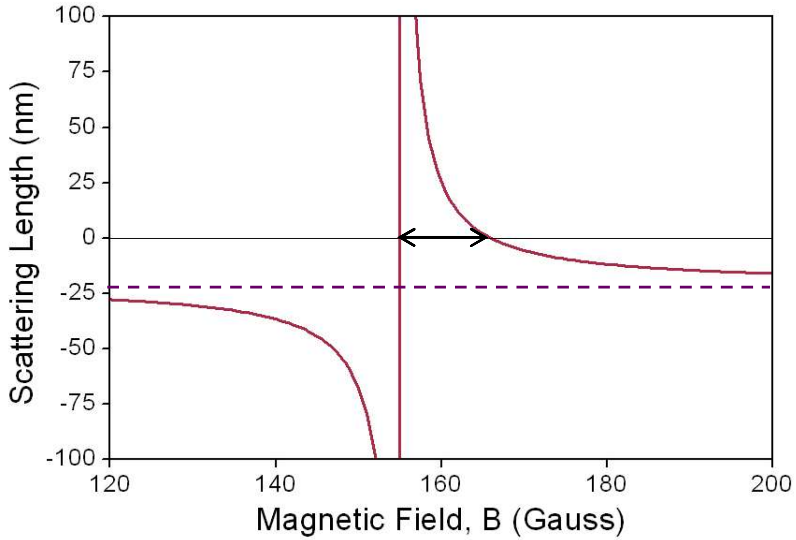
# Feshbach Resonance



# Example: the $^{85}$Rb resonance



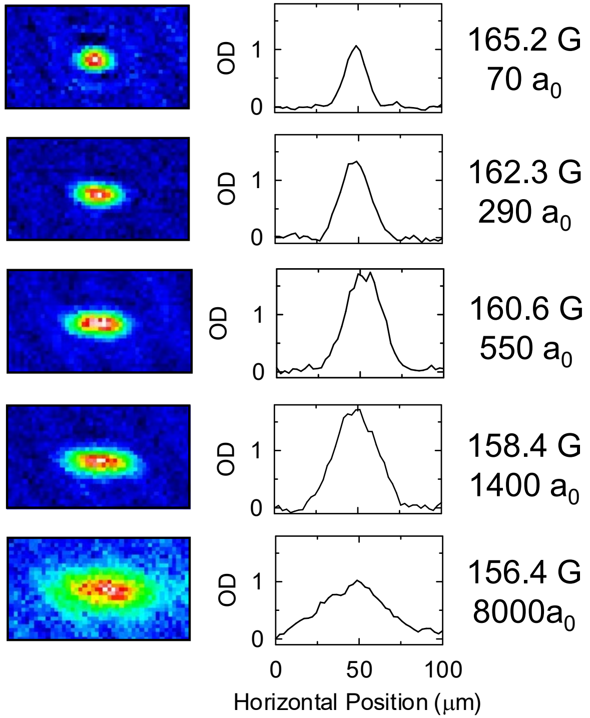



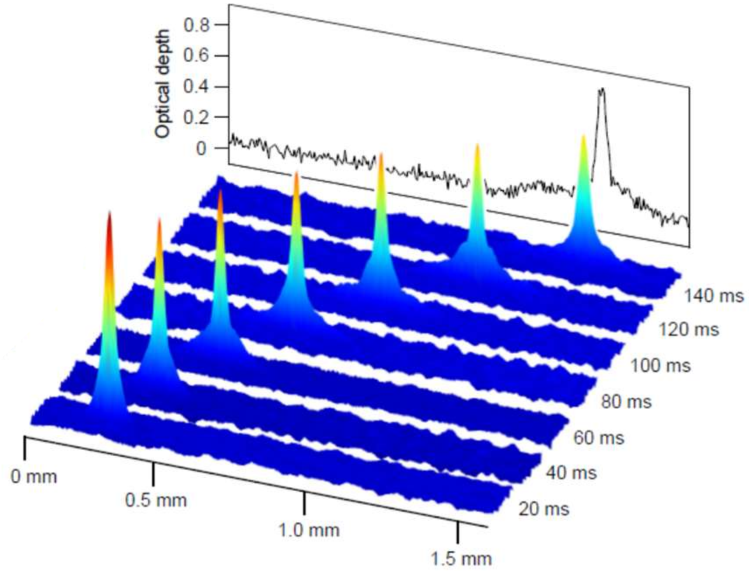
# Tuning the interactions in a BEC

$$i\hbar\frac{\partial}{\partial t}\Phi(\vec{r},t)=\left(-\frac{\hbar^2\nabla^2}{2m}+V_{ext}(\vec{r})+\frac{4\pi\hbar^2 a}{m}|\Phi(\vec{r},t)|^2\right)\Phi(\vec{r},t)$$

Cornish *et al.*, PRL **85**, 1795 (2000)

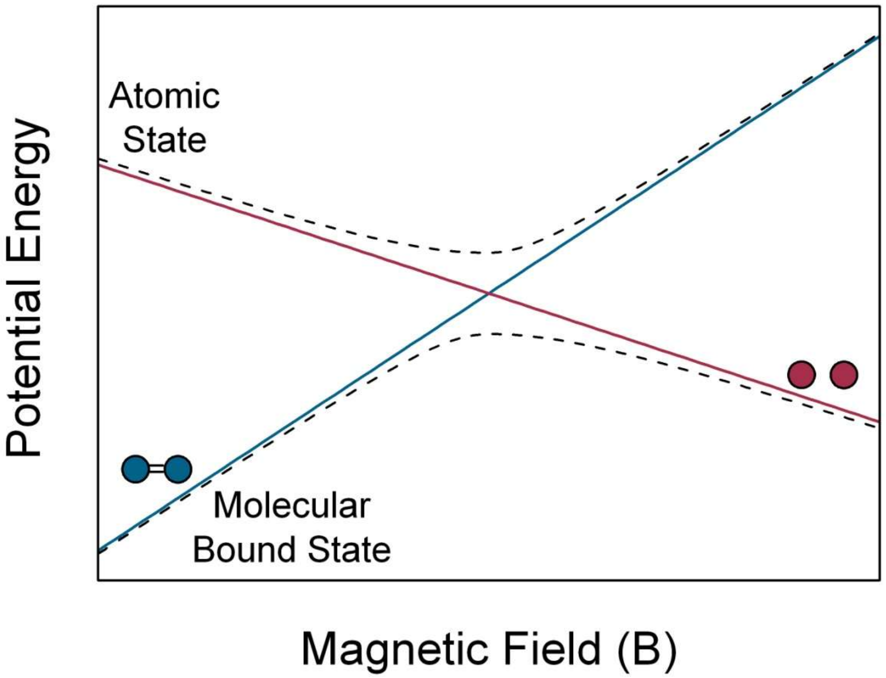



Marchant *et al.*, Nat. Commun. **4**, 1865 (2013)




Soliton: attractive BEC ( -11 $a_0$)

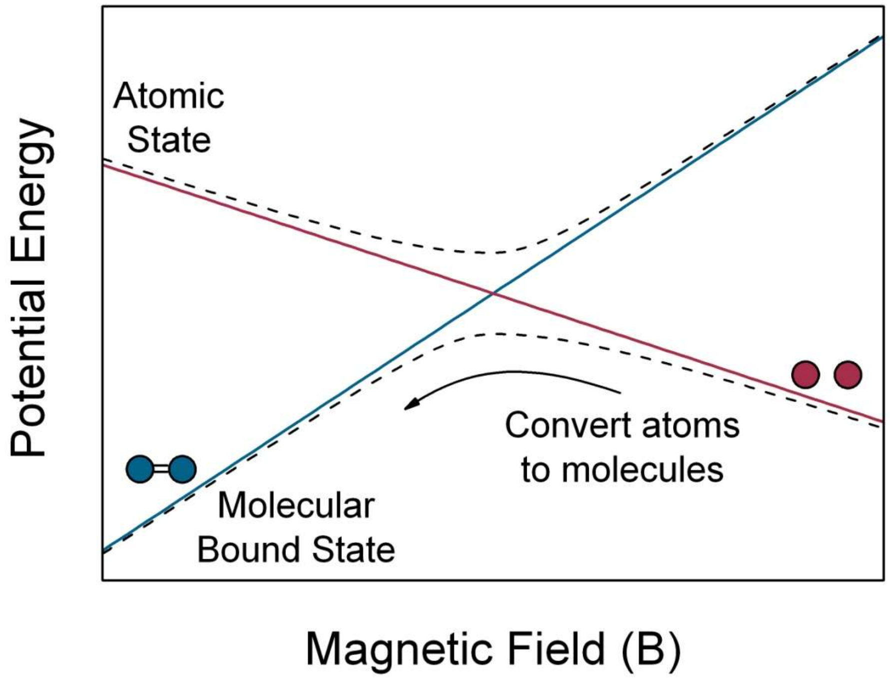
# Magneto-association




But: for atom pairs in lattices and tweezers conversion efficiency can be 100%

# Magneto-association






2-body Landau-Zener:

$$\frac{P_{\text{Mol}}}{P_{\text{Max}}} = 1 - e^{-\delta_{\text{LZ}}}$$

$$\delta_{\text{LZ}} \propto n \left| \frac{a_{\text{bg}} \Delta}{\dot{B}} \right|$$

Density — Sweep Rate

Maximum conversion efficiency depends on PSD: Determines number of suitable two-body pairs.

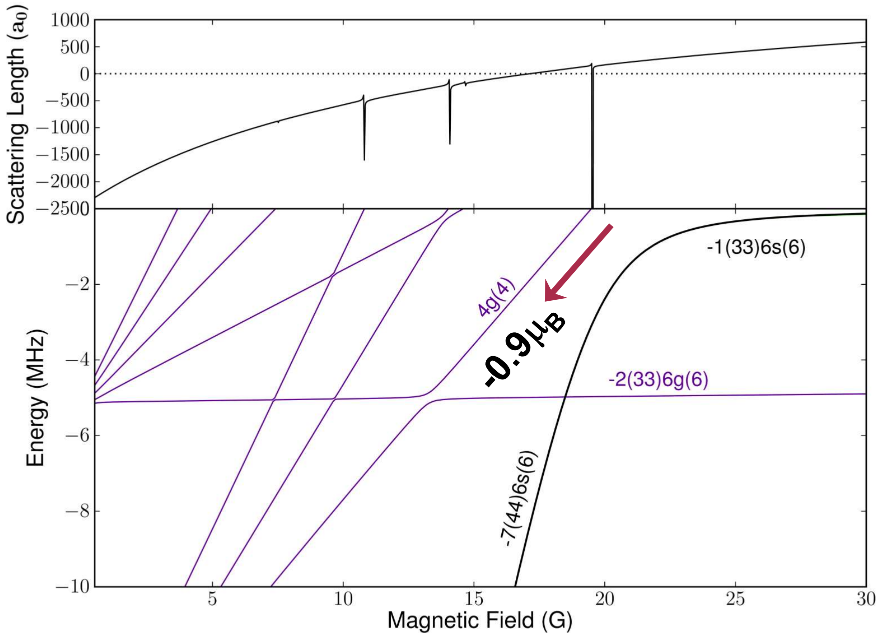
Hodby et al., PRL **94**, 120402 (2005)

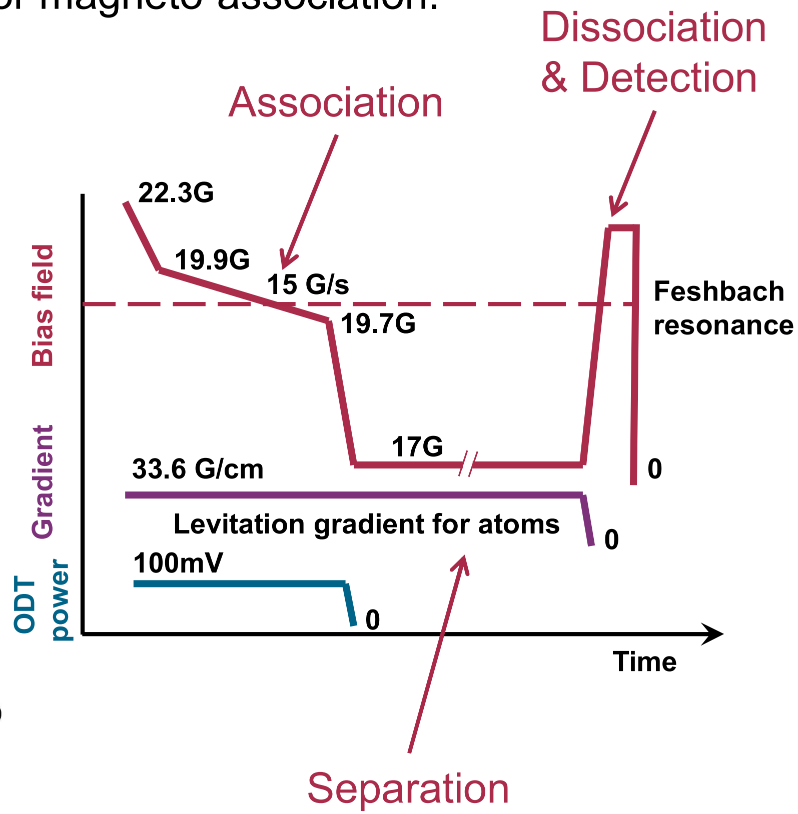
But: for atom pairs in lattices and tweezers conversion efficiency can be 100%

[Also see Kohler et al., Rev. Mod. Phys. **78**, 1311 (2006)]

# A simple example… $Cs_2$

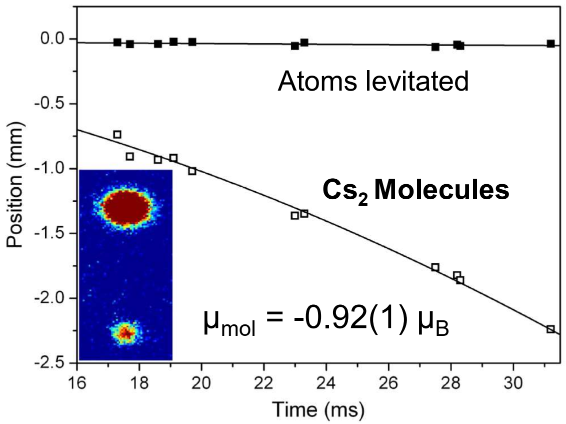
- Use 19.8 G resonance in Cs F=3, $m_F$=+3 for magneto-association.



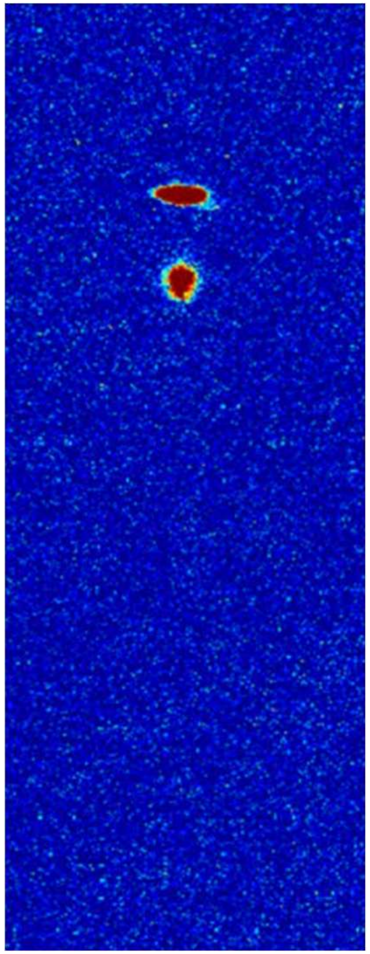



# A simple example… $Cs_2$

- Initially: $T_{Cs}$ = 60 nK, $N_{Cs}$ = 1 x $10^5$, $PSD_{Cs}$ = 1.5
- $N_{Cs_2}$ = 1.3 x $10^4$, Transfer efficiency ~13%




Decreasing magnetic field

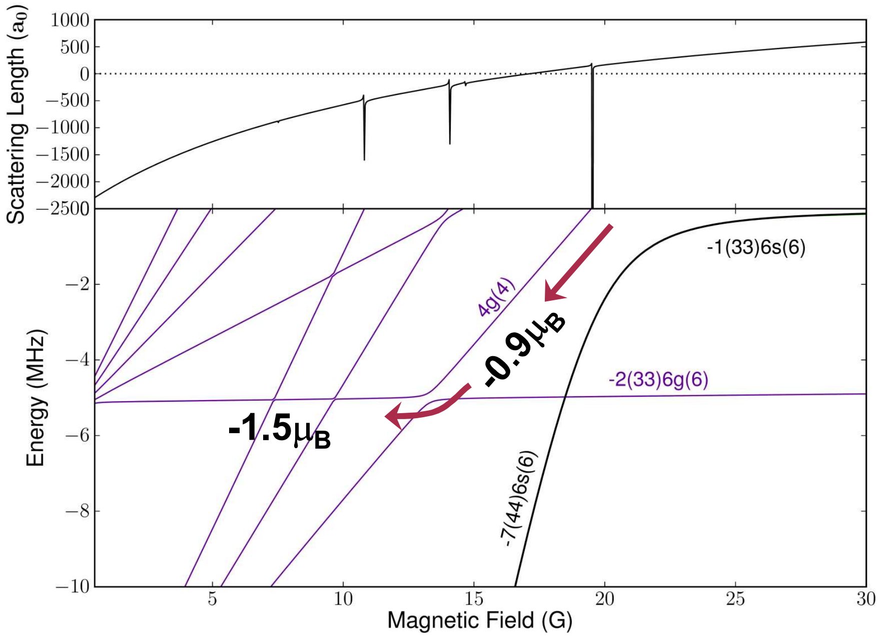


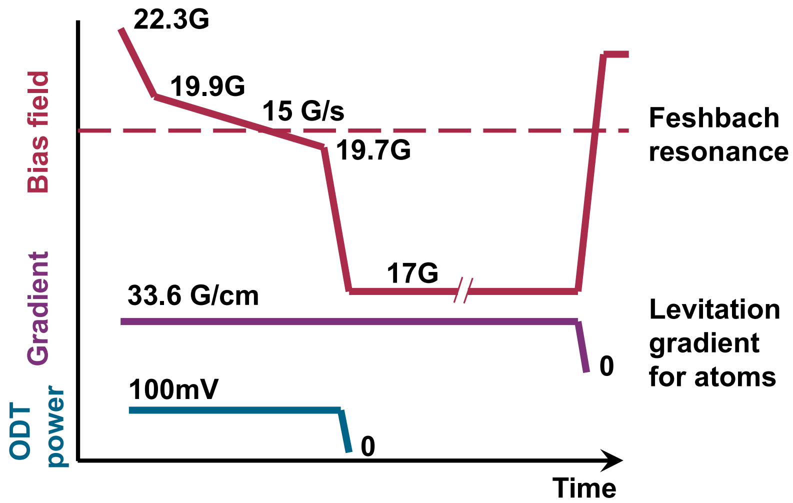
**From expansion: $T_{Cs_2}$ = 60nK**

# A simple example… $Cs_2$

Durham University

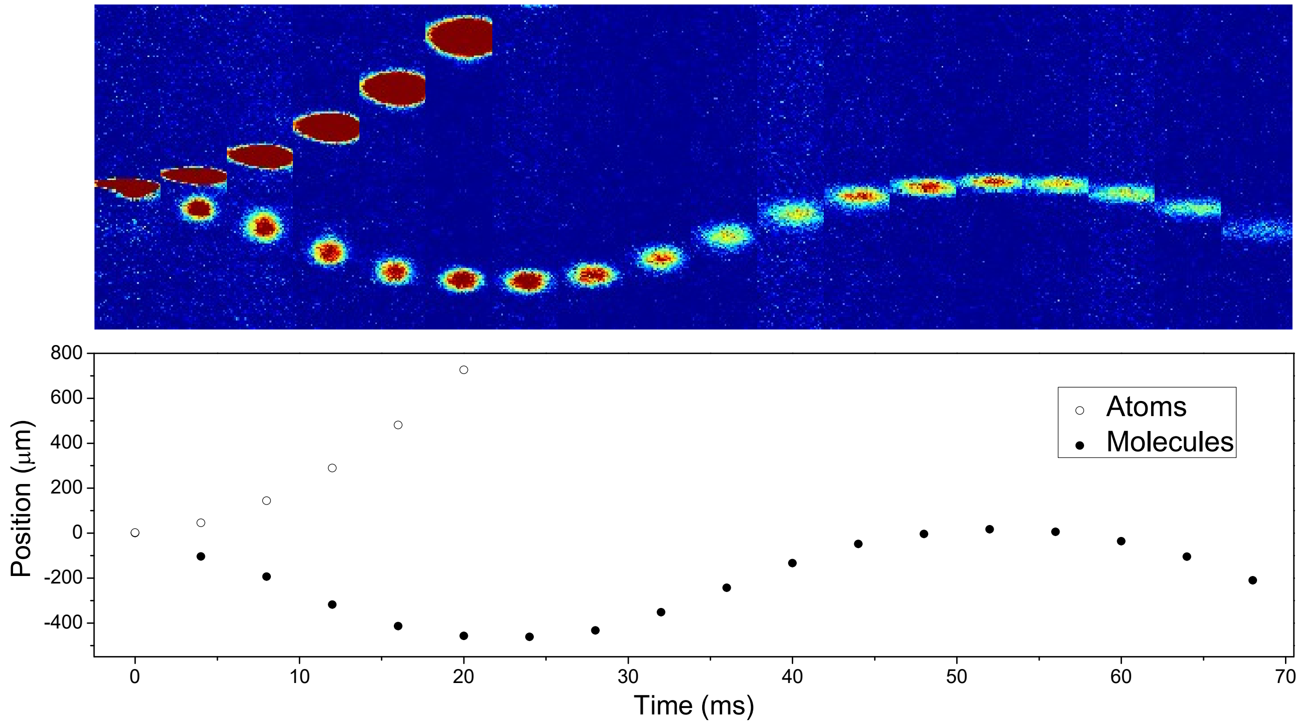
- Use 19.8 G resonance in Cs for magneto-association.



# “Bouncing” $Cs_2$ molecules

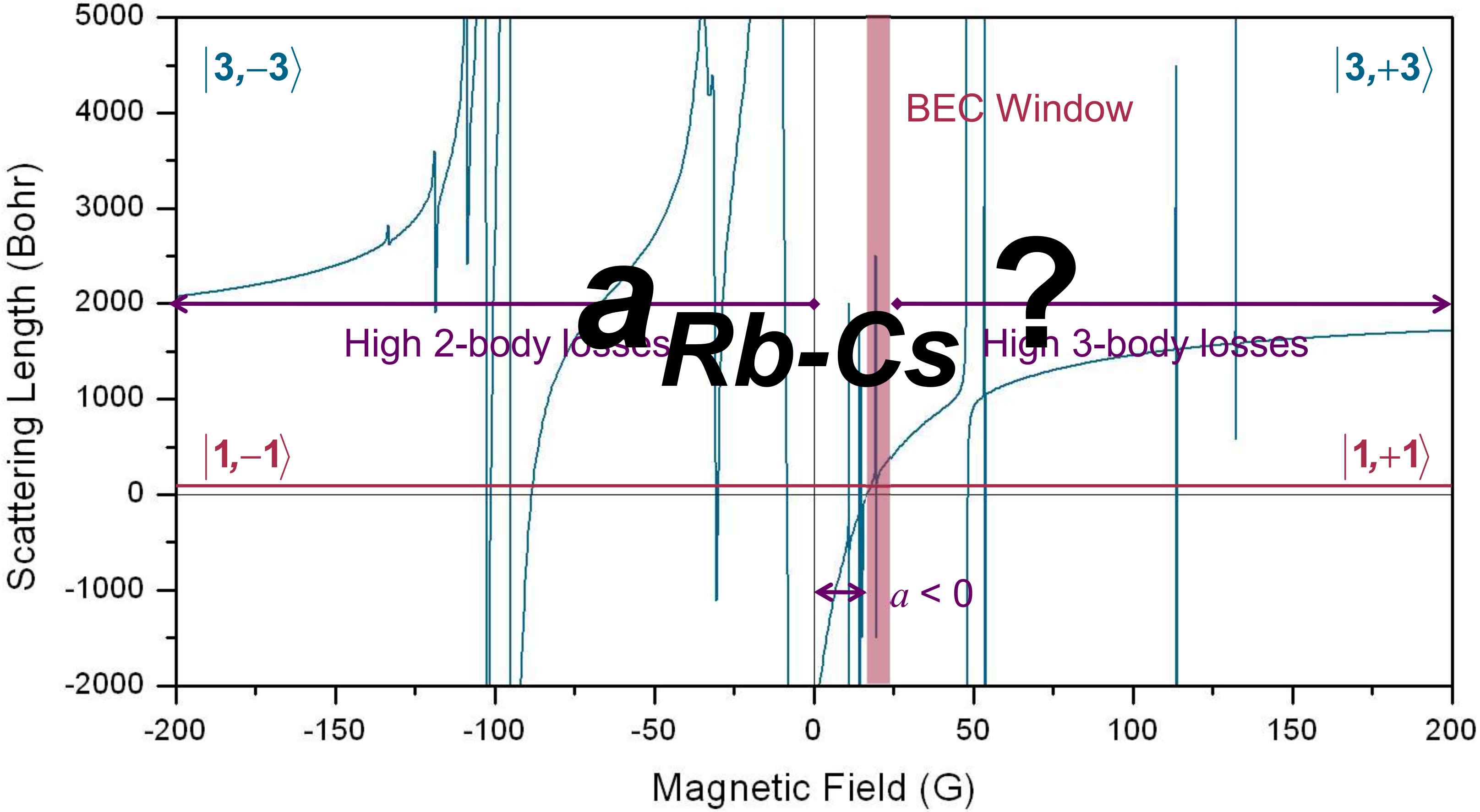





**Can easily navigate bound state spectrum – important for RbCs**

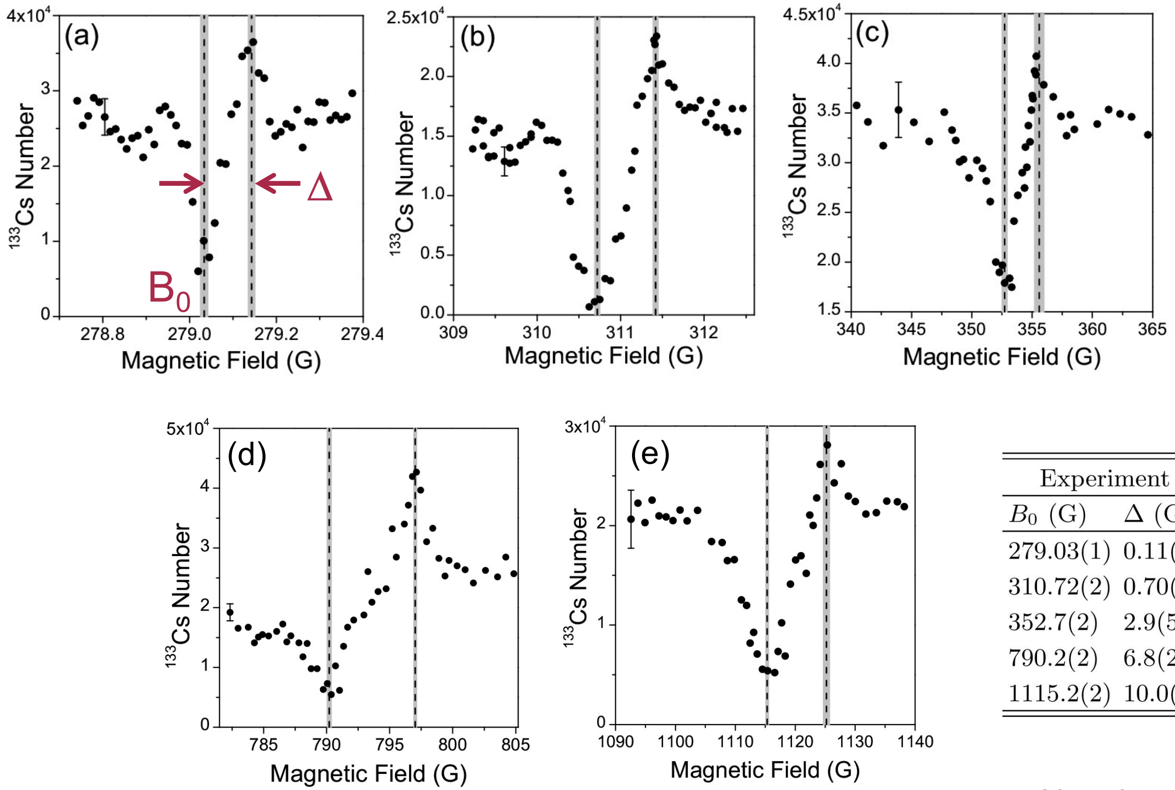
# What about two species?

Challenges
- 3 scattering lengths need to be controlled with 1 magnetic field!
- interspecies scattering length is usually unknown!



# After several years and many measurements…

T. Takekoshi *et al.*, PRA **85**, 032506 (2012)
K. Pilch *et al.*, PRA **79**, 042718 (2009)
M. Köppinger *et al.*, PRA **89**, 033604 (2014)



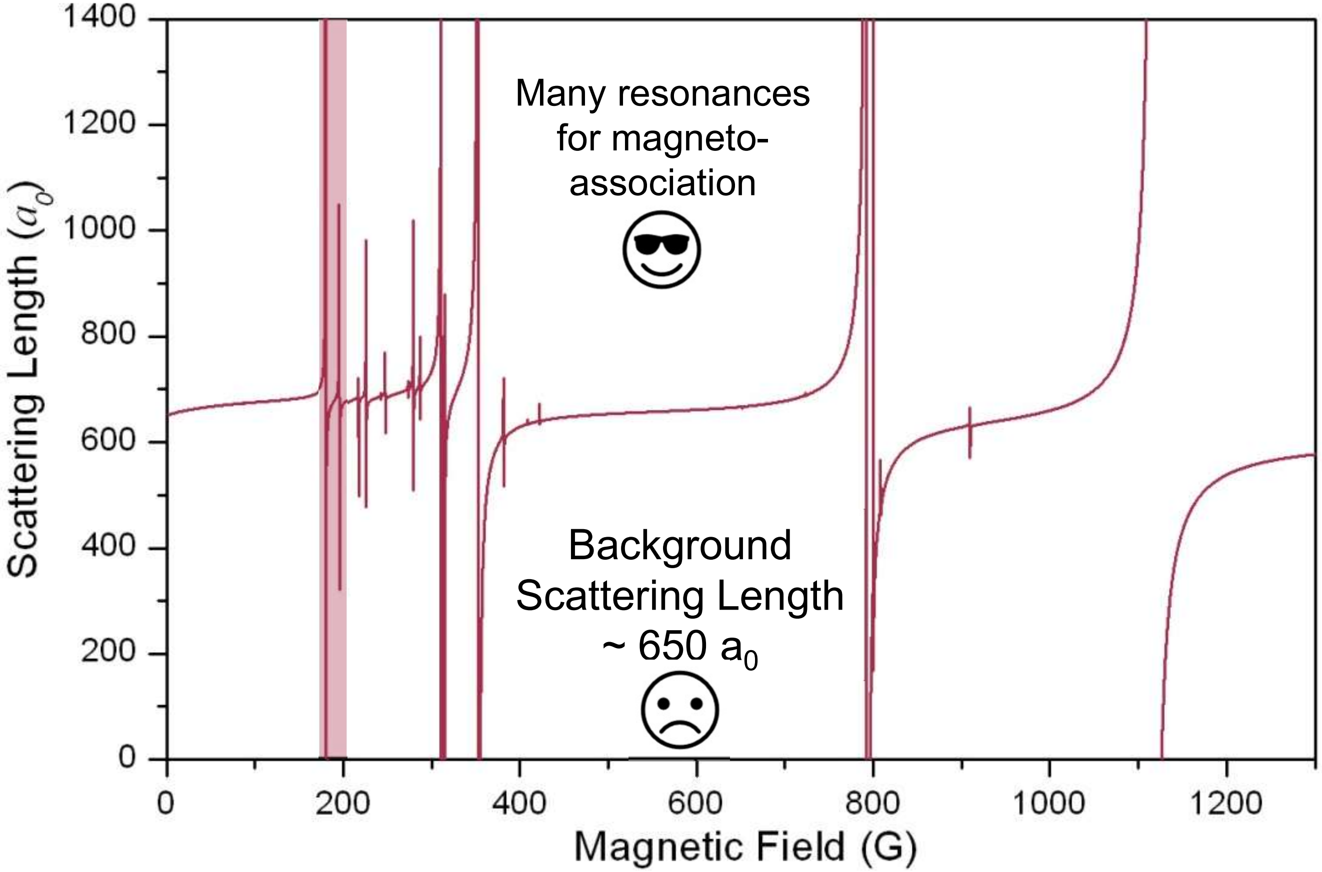

$N_{Rb} = 9 \times 10^4$, $T_{Rb} = 210$nK
$N_{Cs} = 3 \times 10^4$, $T_{Cs} = 260$nK

| Experiment | | Theory | | |
|---|---|---|---|---|
| $B_0$ (G) | $\Delta$ (G) | Quantum labels | $B_0$ (G) | $\Delta$ (G) |
| 279.03(1) | 0.11(1) | $\lvert -6(2,4)s(2,2)\rangle$ | 278.972 | 0.034 |
| 310.72(2) | 0.70(3) | $\lvert -6(2,4)s(1,3)\rangle$ | 310.669 | 0.583 |
| 352.7(2) | 2.9(5) | $\lvert -6(2,4)s(0,4)\rangle$ | 352.706 | 2.206 |
| 790.2(2) | 6.8(2) | $\lvert -5(2,3)s(2,2)\rangle$ | 791.762 | 4.220 |
| 1115.2(2) | 10.0(6) | $\lvert -5(2,3)s(1,3)\rangle$ | 1116.554 | 8.936 |

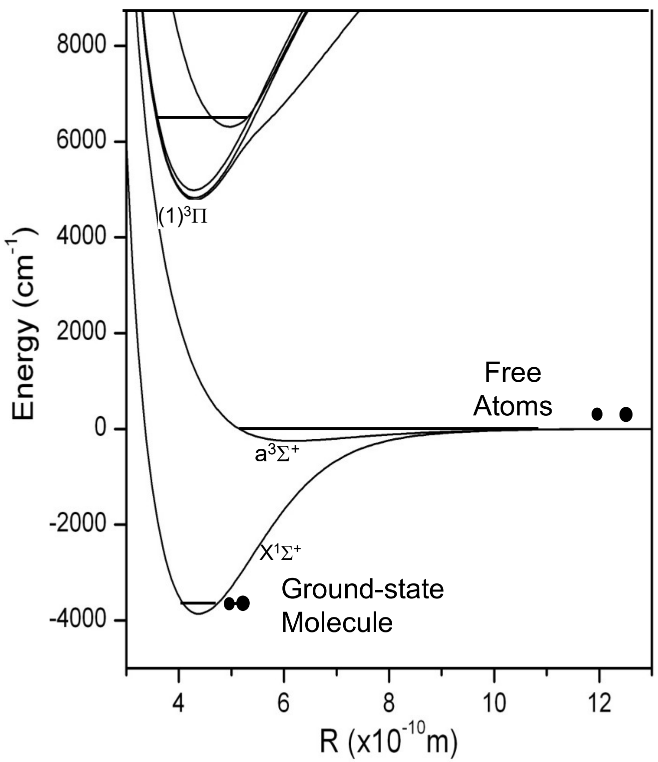
Notation: $\lvert n(f_{Rb}, f_{Cs})L(m_{Rb}, m_{Cs})\rangle$

# Rb-Cs scattering length

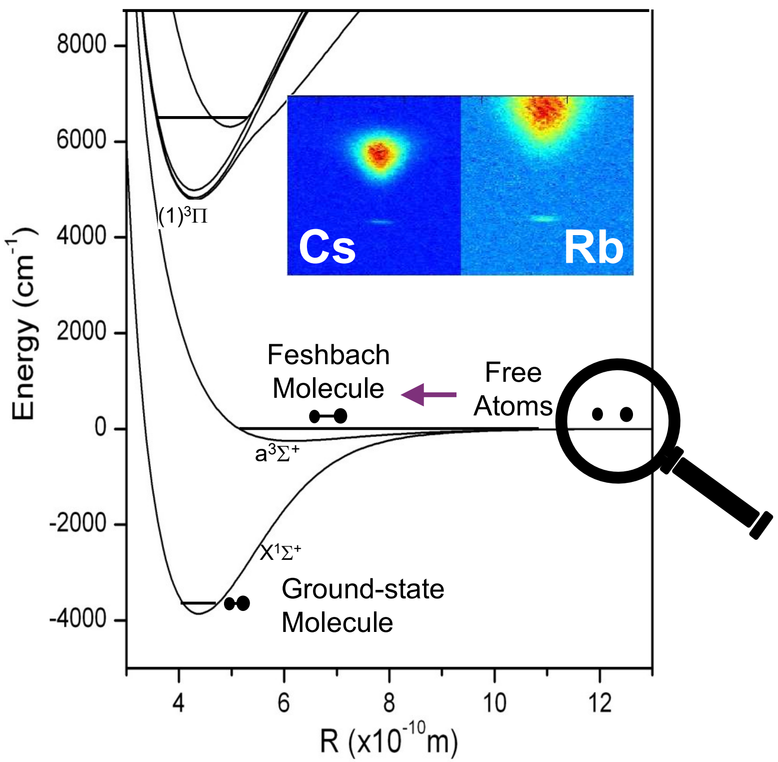
T. Takekoshi *et al.*, PRA **85**, 032506 (2012)
K. Pilch *et al.*, PRA **79**, 042718 (2009)



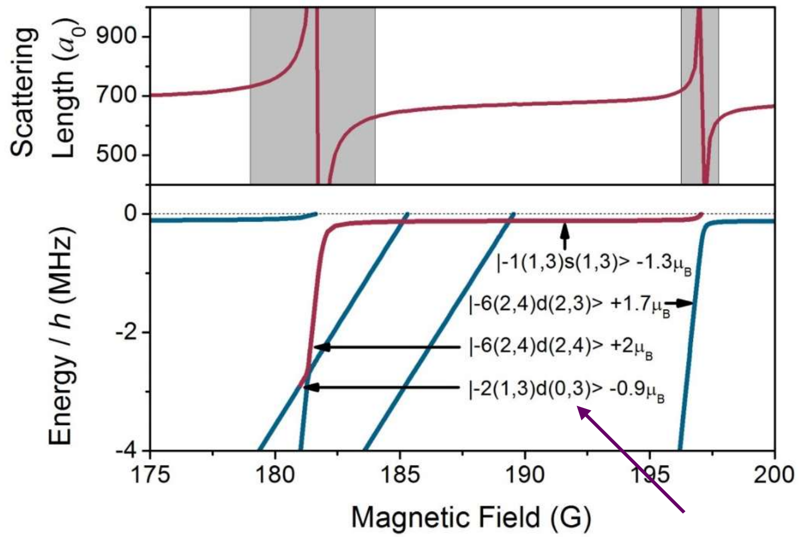
# Entering the molecular world



# Entering the molecular world




Feshbach resonaces & magnetoassociation:
gateway to weakly bound molecules




$|n(f_{\mathrm{Rb}}, f_{\mathrm{Cs}})L(m_{f_{\mathrm{Rb}}}, m_{f_{\mathrm{Cs}}})\rangle$

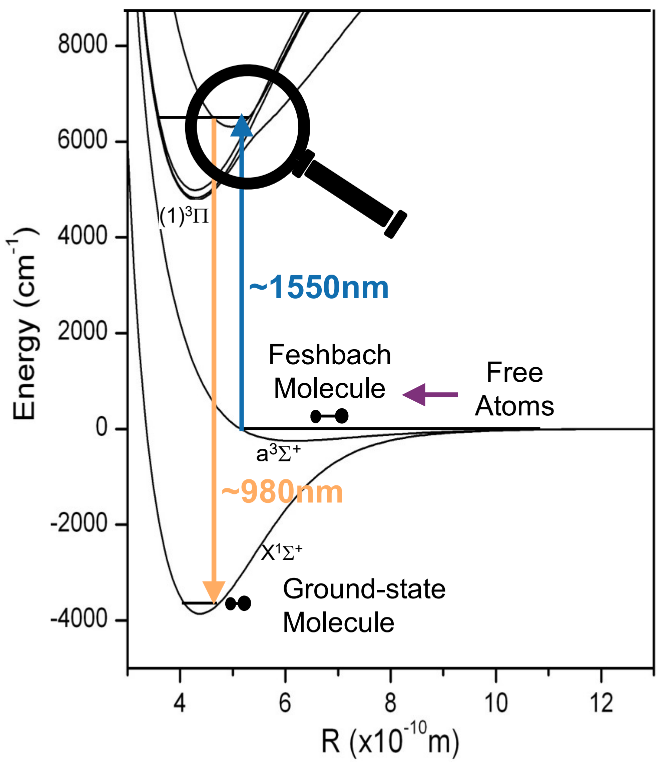
Produce up to 5000 molecules

T = 1.2 μK, $\langle n \rangle \approx 8 \times 10^{10}$ cm$^{-3}$

in the |-6 ⟩ state in a pure optical trap

# Transfer to the ground state



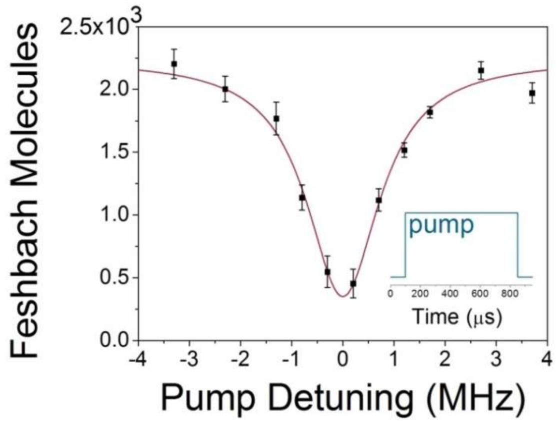


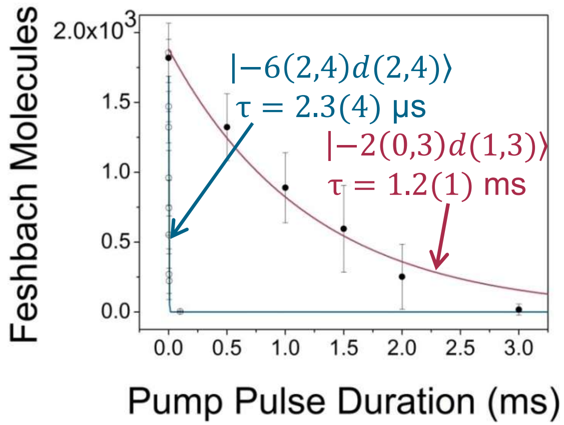

Use Stimulated Raman Adiabatic Passage (STIRAP) to transfer to the ground state:

Need to find state with mixed singlet-triplet character

For STIRAP use

$|\Omega' = 1, v' = 29, J' = 1\rangle$ of $b^3\Pi$:

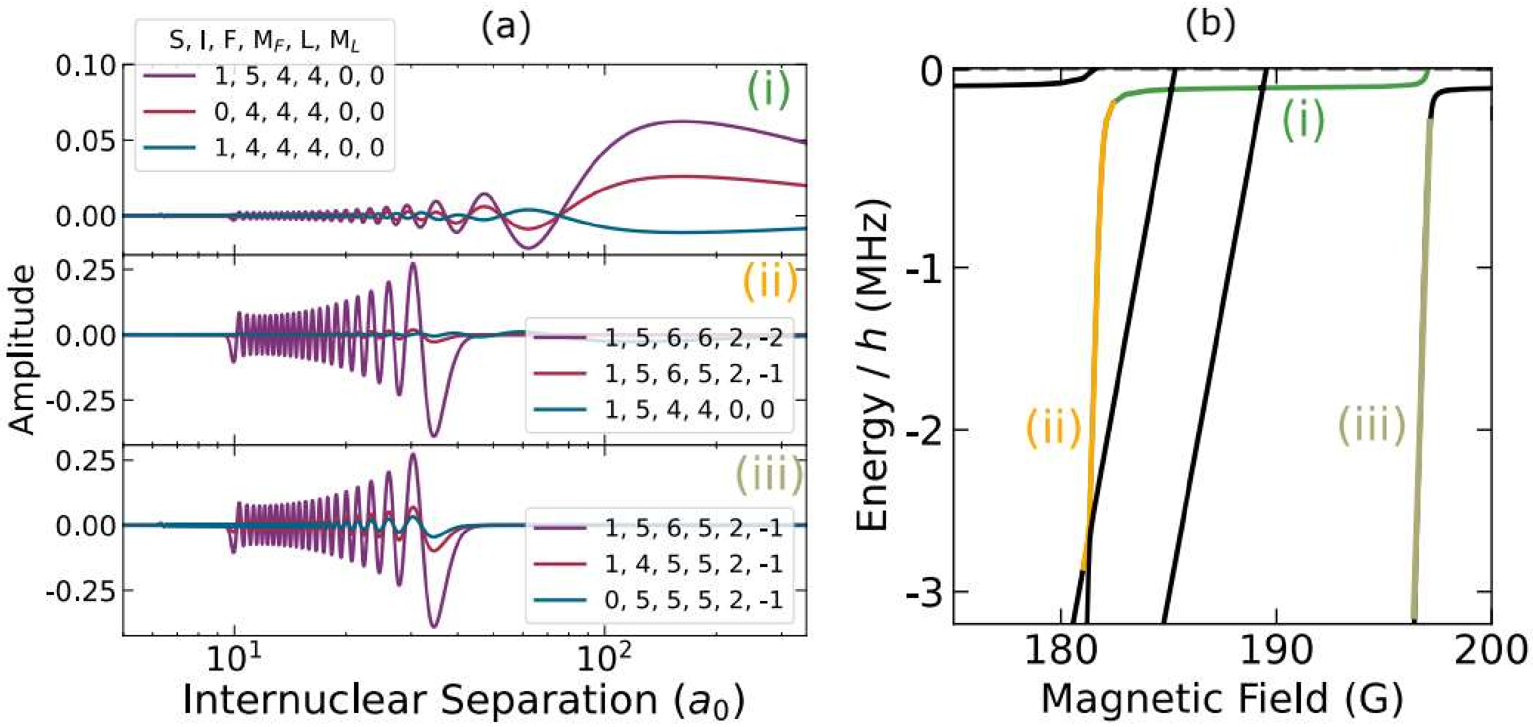



Admixture of $A^1\Sigma^+$ allows coupling to g.s.

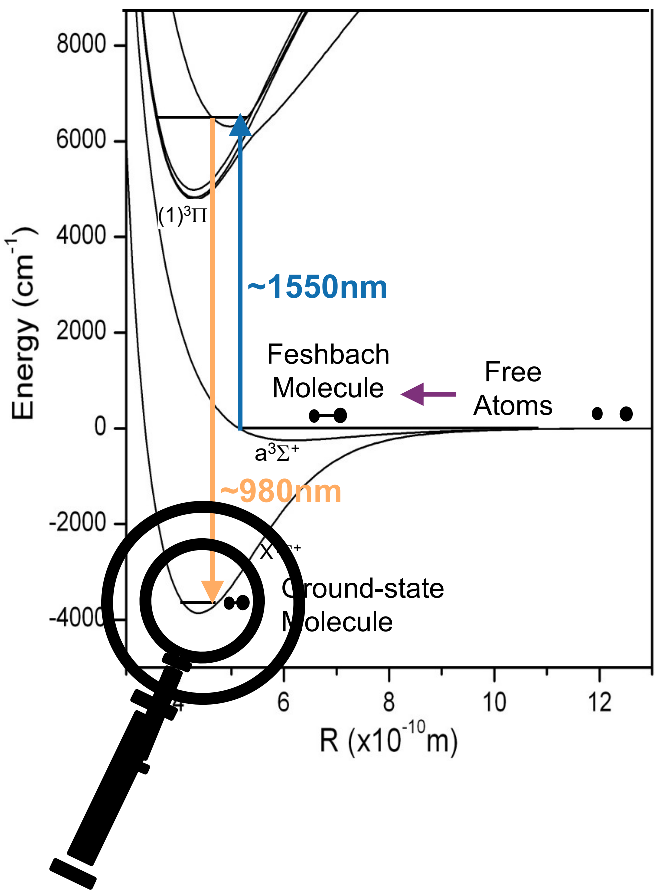
# Highlights importance of Feshbach state

Wavefunctions show the three channels with the largest contributions to each state, out of a basis of 48 channels satisfying $M_F + M_L = 4$.



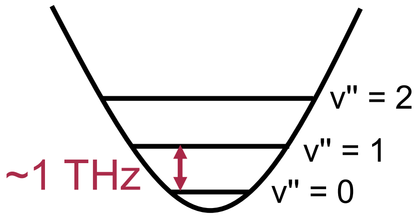

Enhanced short range character is crucial

# Transfer to the ground state

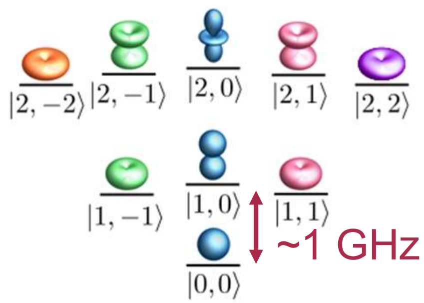



Use Stimulated Raman Adiabatic Passage (STIRAP) to transfer to the ground state:

**Vibration:**



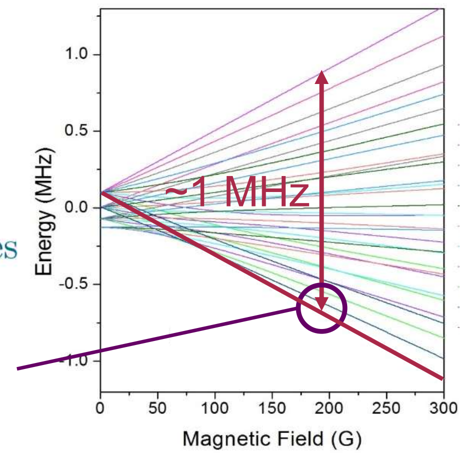

**Rotation:**




**Hyperfine:**

$$I_{\mathrm{Rb}} = \frac{3}{2}, I_{\mathrm{Cs}} = \frac{7}{2}$$

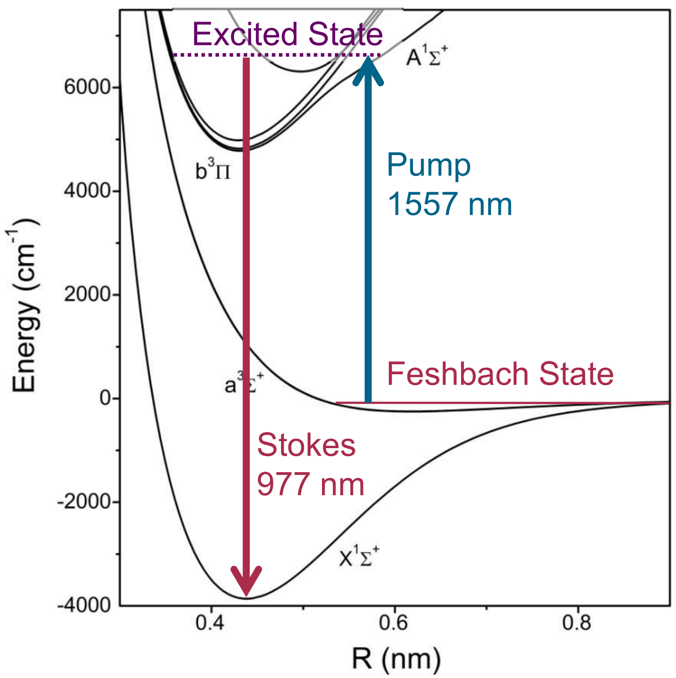
$$(2I_{\mathrm{Rb}}+1)(2I_{\mathrm{Cs}}+1) = 32 \text{ states}$$



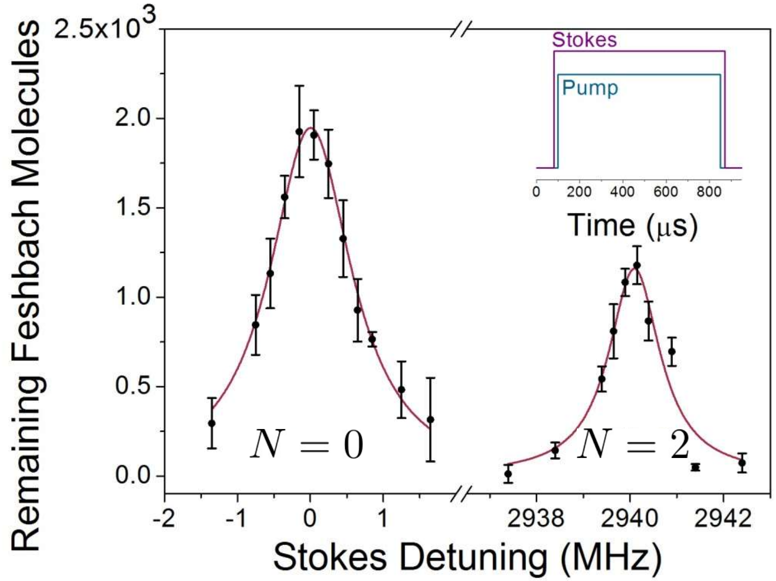

Address absolute lowest state ($m_F$ = +5)

# Two photon optical spectroscopy

Admixture of $A^1\Sigma^+$ allows coupling to g.s.




For STIRAP use
$|\Omega' = 1, v' = 29, J' = 1\rangle$ of $b^3\Pi$:

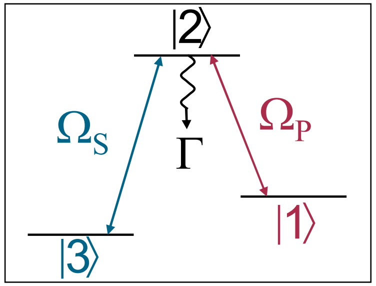



Difference between $N$ = 0 and $N$ = 2
matches expected rotational splitting

Molony *et al.*, PRL **113**, 255301 (2014)

# Transfer to the ground state

Map onto a simple 3-level system:



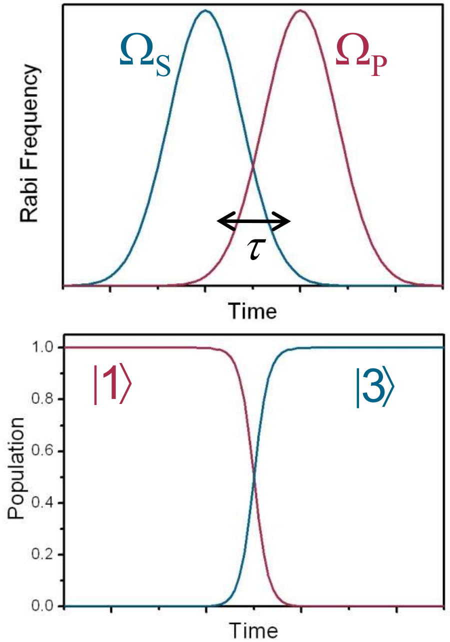

Ignoring the decay, the Hamiltonian in the RWA is:

$$\hat{H} = \begin{pmatrix} 0 & \Omega_P(t) & 0 \\ \Omega_P(t) & \Delta_P & \Omega_S(t) \\ 0 & \Omega_s(t) & 2(\Delta_P - \Delta_S) \end{pmatrix}$$

One of the eigenstates is a *dark* state:

$$|a^0\rangle = \cos\theta\,|1\rangle - \sin\theta\,|3\rangle$$

$$\tan\theta = \frac{\Omega_P(t)}{\Omega_S(t)}$$




Relative Laser linewidth

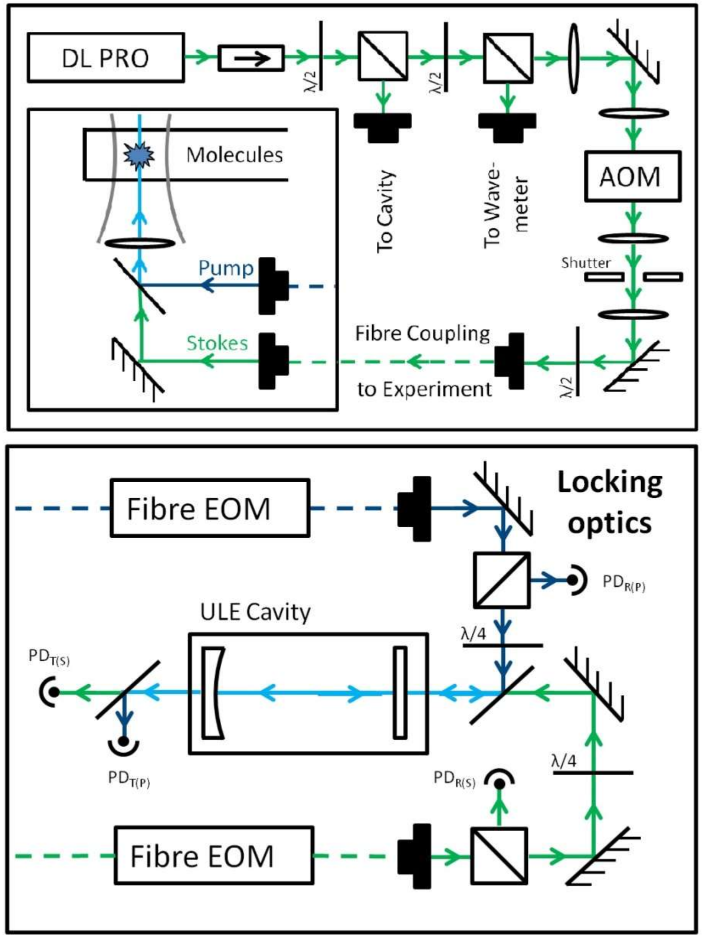
For efficient transfer:

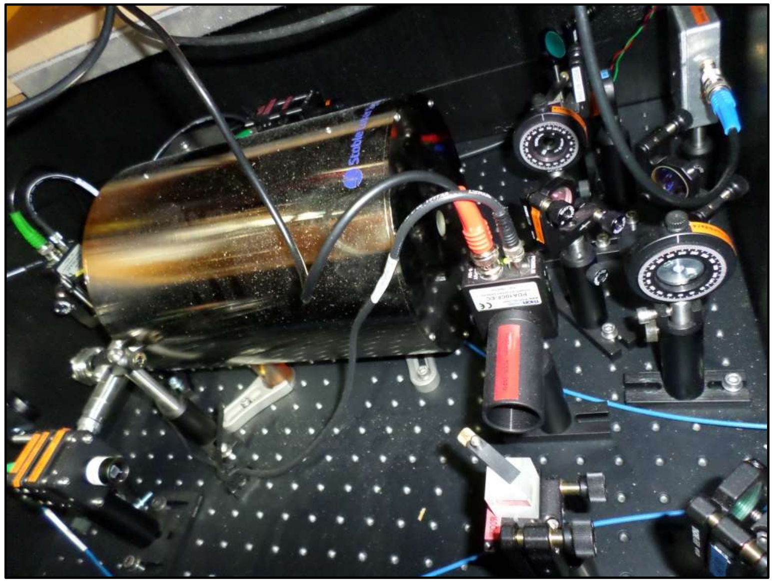
Adiabaticity Decoherence

$$\left(\frac{\Omega_P^2+\Omega_S^2}{\pi^2\Gamma}\right) >> \frac{1}{\tau} >> D$$

<5 μs 10 kHz

# Laser system for STIRAP



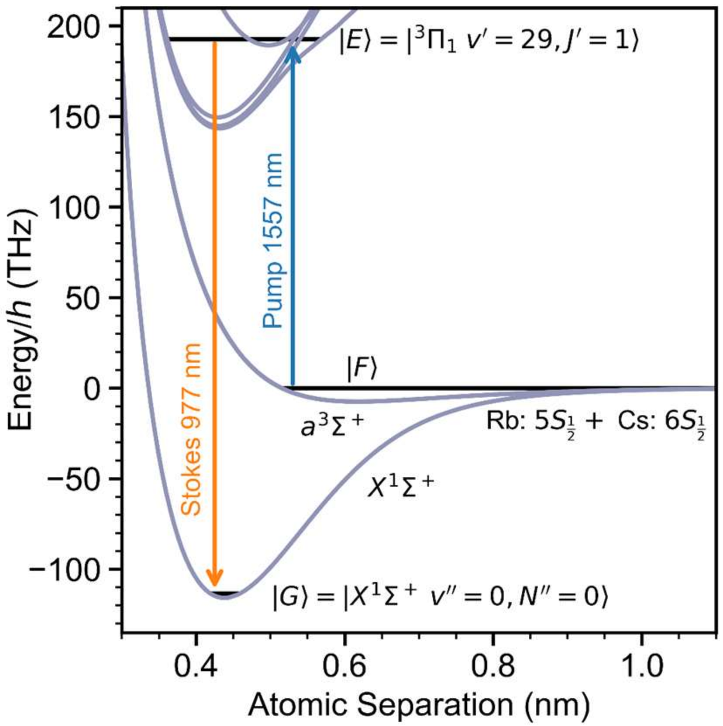



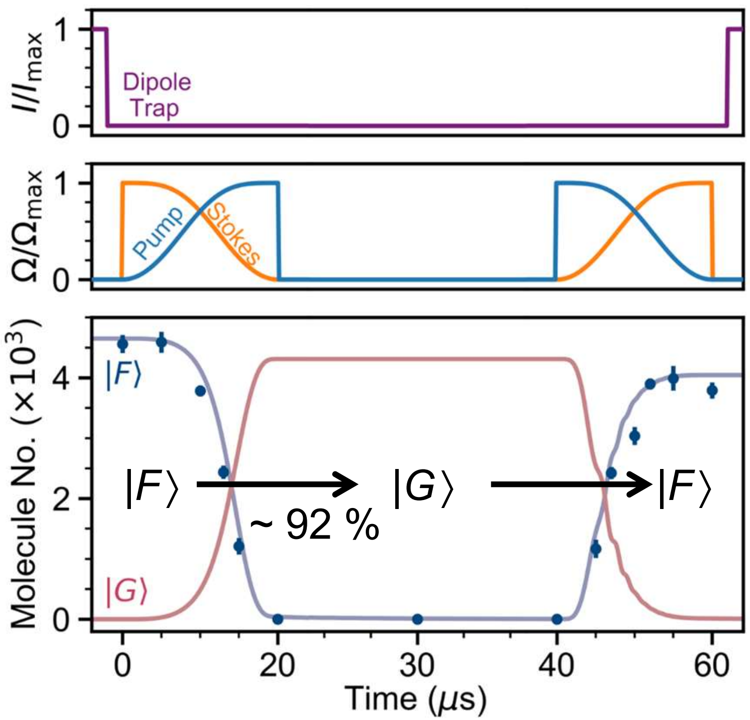
| Test wavelength (nm) | 977 | 1557 |
|---|---|---|
| Zero-expansion (°C) | 35 | – |
| Length( mm) | 100.13958(7) | 100.15369(7) |
| FSR ( MHz) | 1496.873(1) | 1496.662(1) |
| Finesse | $1.37(6) \times 10^4$ | $1.19(6) \times 10^4$ |
| Mode linewidth ( kHz) | 109(5) | 126(5) |

**Laser linewidths < 1 kHz**

# STIRAP to ground state

Durham University

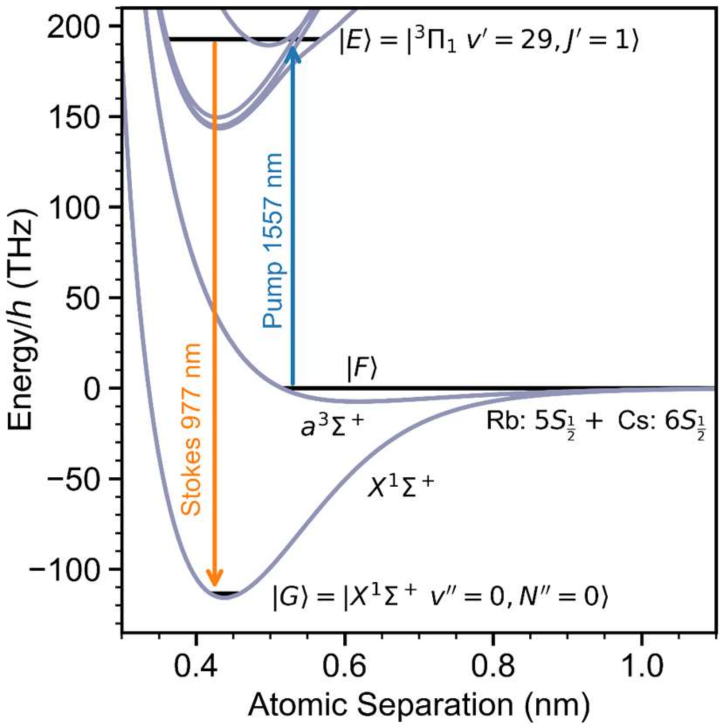


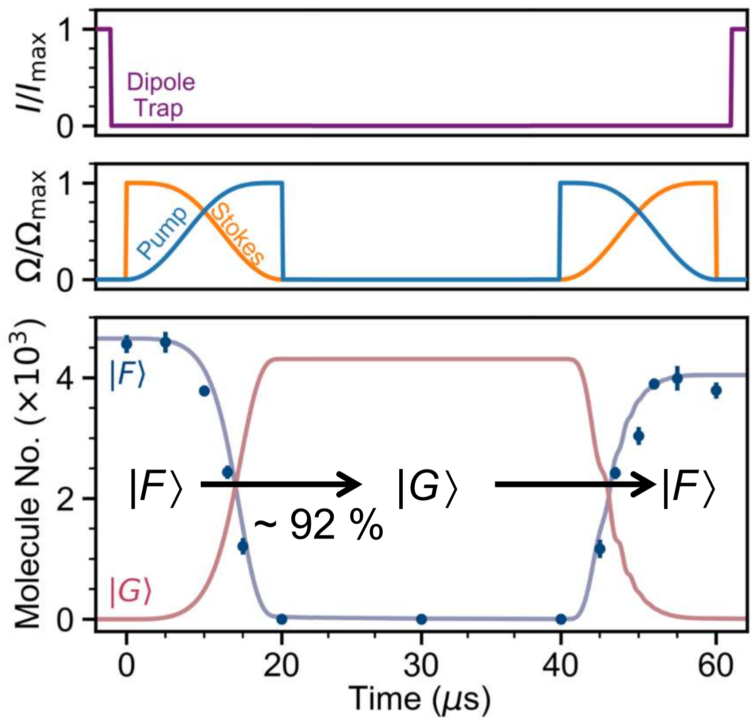




Transfer to the **vibrational, rotational and hyperfine ground state**:

$v = 0$, $N = 0$, $M_F = +5$

# STIRAP to ground state




**Final Molecule Sample:**

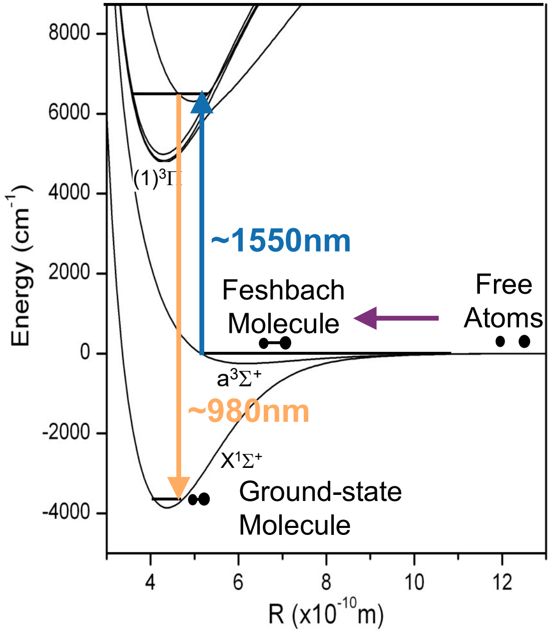
$N$ = 4000, $T$ = 1.5 μK

$n_{pk} \approx 2 \times 10^{11}$ cm$^{-3}$

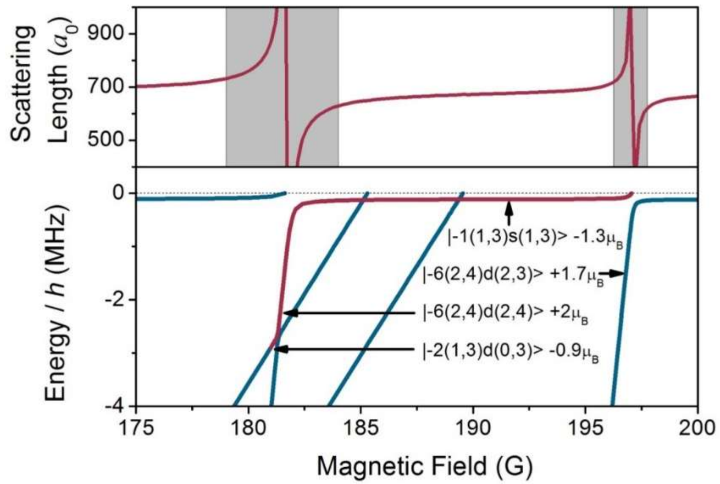
# Summary: making RbCs molecules

Durham University

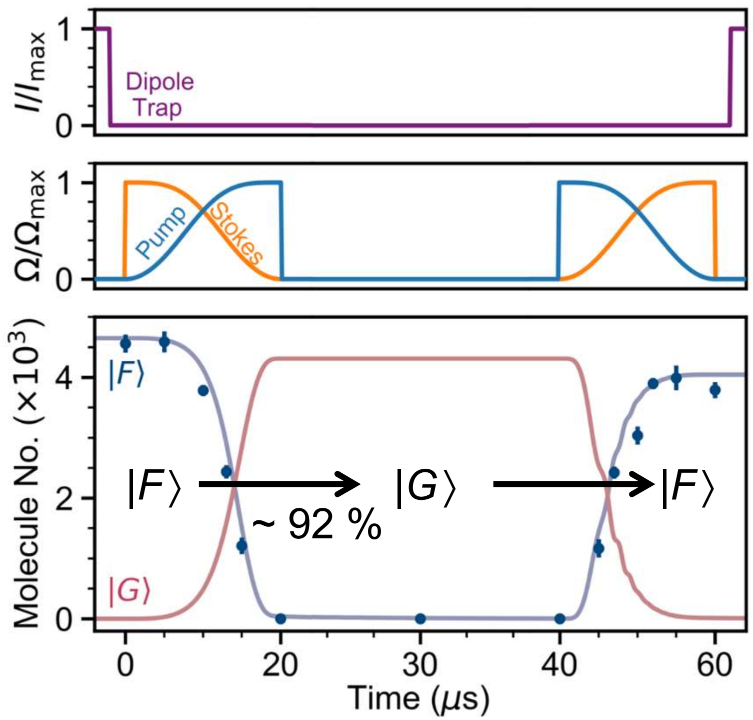
Start with Rb + Cs atoms




Magnetoassociation




STIRAP at ~181 G




Takekoshi et al., PRL **113**, 205301 (2014)
Molony et al., PRL **113**, 255301 (2014)

# Questions?