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Rotational properties of two interacting ultracold polar molecules

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Outline

We study two interacting ultracold **polar molecules** of arbitrary geometry by taking their **internal rotation** into account.

1. Ultracold molecules
2. Internal rotation of molecules
3. Two interacting polar molecules
4. Conclusions

Ultracold atoms

- **Cooling and trapping** techniques have produced a wealth of opportunities in the realisation of **ultracold atoms** ($T<\mu K$).
  W. D. Phillips, Rev. Mod. Phys. **70**, 721 (1998). I. Bloch *et al.*, Rev. Mod. Phys. **80**, 885 (2008).
- Experimentalists have continued achieving more complex configurations of ultracold atom gases.
- **Alkali** atoms offer an unprecedented level of controllability, enabling us to **simulate** other quantum systems.
  I. Bloch, J. Dalibard and S. Nascimbène, Nat. Phys. **8**, 267 (2012).
  C. Gross and I. Bloch, Science **357**, 995 (2017).

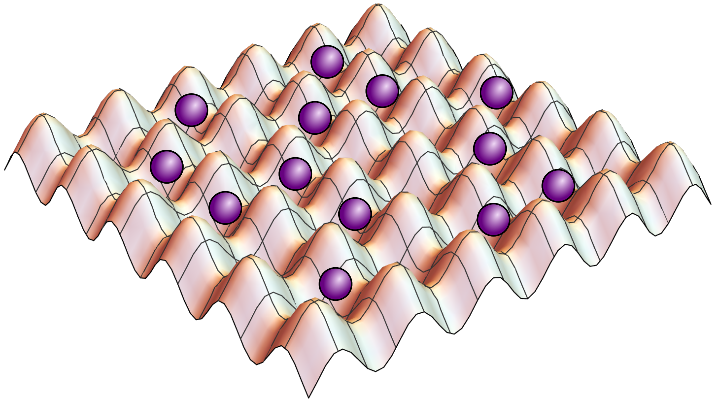


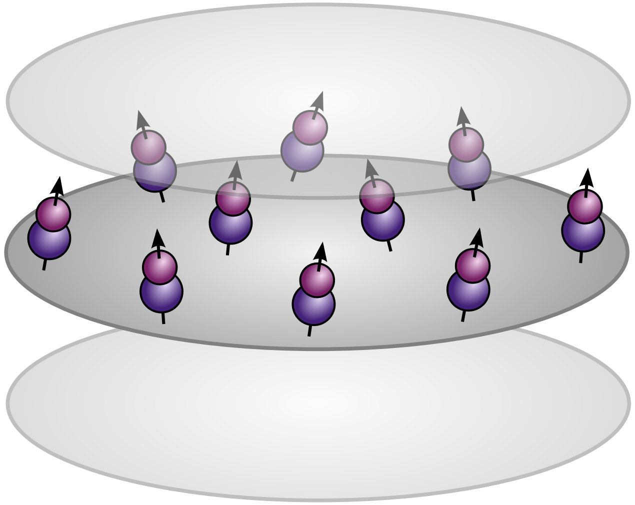
Illustration of ultracold atoms trapped in a two-dimensional optical lattice.

Ultracold molecules

- The last two decades have seen rapid progress in the realisation of **cold and controlled molecules**.
  G. Quéméner and P. S. Julienne, Chem. Rev. **112**, 4949 (2012). J. L. Bohn *et al*., Science **357**, 1002 (2017).

- Gases of ultracold **alkali dimers** (KRb, RbCs, etc.) have already been produced.
  K.-K. Ni *et al*., Science **322**, 231235 (2008). T. Takekoshi *et al.*, Phys. Rev. Lett. **113**, 205301 (2014).

- Molecular dimers are produced by binding two atoms with **Feshbach resonances** techniques.
  T. Köhler, K. Góral, and P. S. Julienne, Rev. Mod. Phys. **78**, 1311 (2006).



Ultracold molecules

- Recent progress on **laser cooling** has started enabling the **direct** cooling of molecules.

- A few **non-alkali** molecules (CaF, YO, SrOH, CaOH, $CaOCH_3$, etc) have already been cooled to the ultracold regime.
  S. Truppe *et al.*, Nat. Phys. **13**, 1173(2017). S. Ding *et al.*, Phys. Rev. X **10**, 021049 (2020).
  I. Kozyryev *et al.*, Phys. Rev. Lett. **118**, 173201 (2017). N. B. Vilas *et al*., Nature **606**, 70 (2022).
  D. Mitra *et al*., Science **369**, 1366 (2020).

- Roadmaps for realising more and more complex ultracold molecules have been proposed.
  T. A. Isaev and R. Berger, PRL. **116**, 063006 (2016).
  B. L. Augenbraun *et al.*, PRX **10**, 031022 (2020).

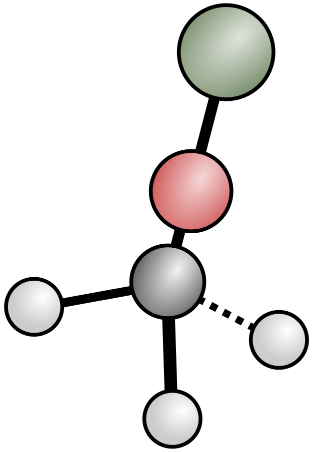


Illustration of a $CaOCH_3$ molecule.

Ultracold molecules

- Molecules offer rich physics due to their complex **internal structure**.

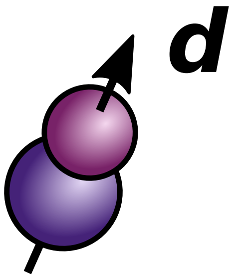
- Cold molecules have many potential applications:

  - Quantum computing.
    D. DeMille, Phy. Rev. Lett. **88**, 067901 (2002). P. D. Gregory *et al.*, Nature Physics **17**, 1149 (2021).

  - Probing fundamental physics.
    J. Baron *et al.*, Science **343**, 269 (2014).

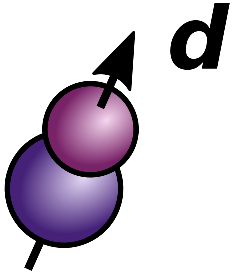
  - Dipolar cold quantum gases.
    S. A. Moses *et al.*, Nat. Phys **13**, 13 (2017).

- Many of these applications rely on the **polar** nature of most molecules.



Polar molecules

- We are interested in molecules with a **permanent electric dipole moment** *d*.
- They interact with external electric fields $\mathcal{E}$,

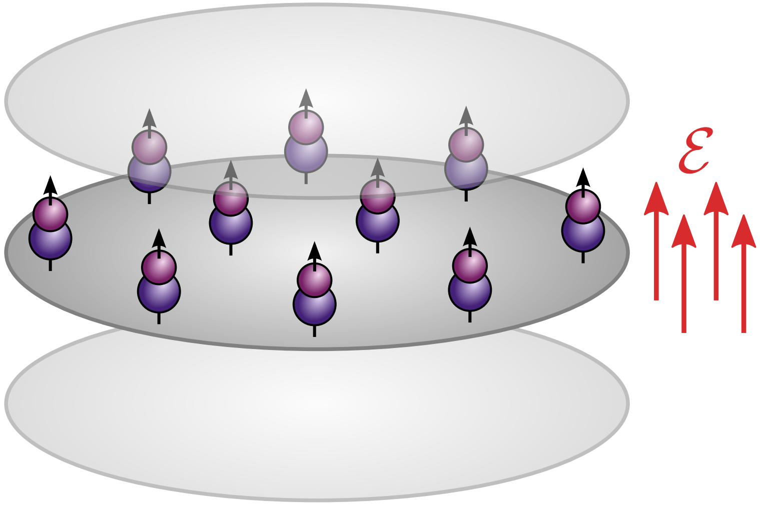


$$H_{\mathrm{dc}} = -\boldsymbol{d} \cdot \boldsymbol{\mathcal{E}}\,.$$

*Additional terms can consider an induced dipole moment.

- Polar molecules can be controlled with electric fields.
- They can be used to realise **ultracold dipolar gases.**

*Dipolar gases can also be realised with magnetic or Rydberg atoms.



Dipole-dipole interaction

- The interaction between dipoles is **long-range** and **anisotropic**

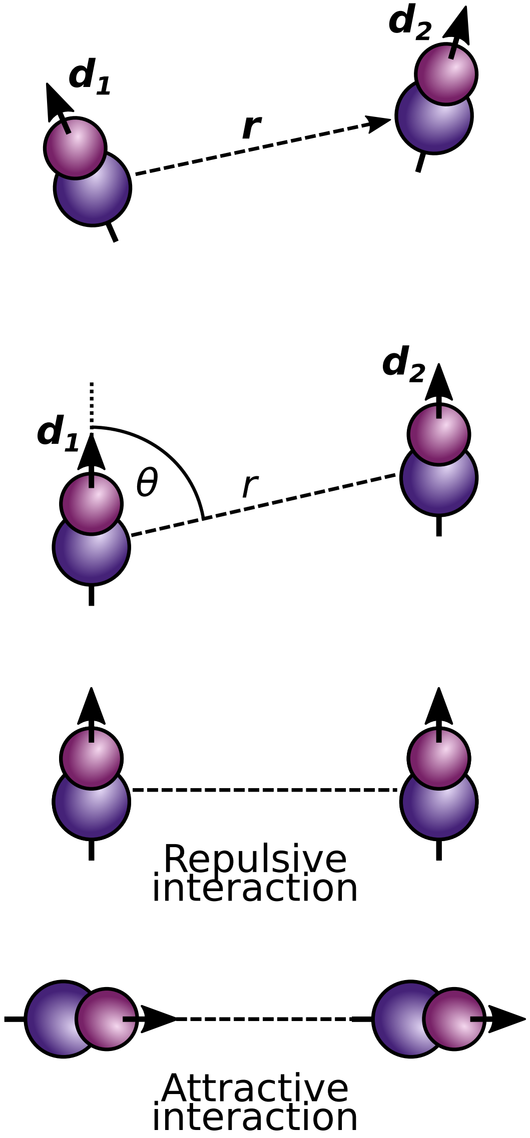
$$V_{\mathrm{dd}} = \frac{(\boldsymbol{d}_1 \cdot \boldsymbol{d}_2) r^2 - 3(\boldsymbol{d}_1 \cdot \boldsymbol{r})(\boldsymbol{d}_2 \cdot \boldsymbol{r})}{r^5} \,.$$

- If the dipoles are **polarised in the same direction**, it takes the simple form

$$V_{\mathrm{dd}} = \frac{1 - 3\cos\theta}{r^3} d^2 \,.$$

- The dipolar interaction produces rich physics, such as **crystalline** and **droplet** phases.

Lahaye *et al.*, Rep. Prog. Phys. **72**, 126401 (2009).



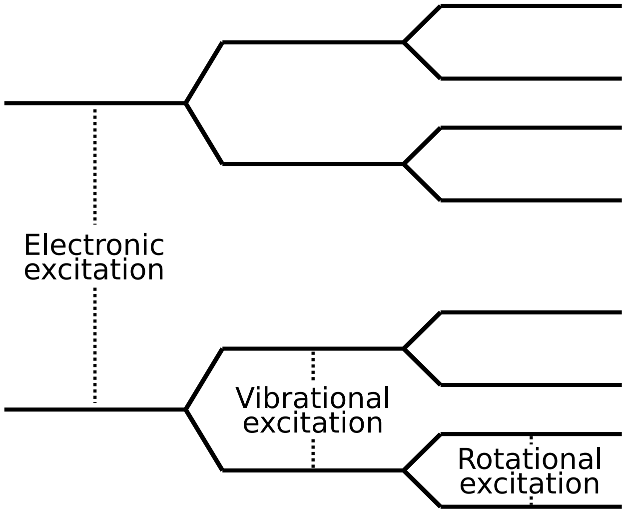
Outline

1. Ultracold molecules
2. **Internal rotation of molecules**
3. Two interacting polar molecules
4. Conclusions

Molecular degrees of freedom

- Molecules are much more complex than atoms.
- They have several **internal degrees of freedom.**

  L. D. Carr *et al.*, New J. Phys. **11** 055049 (2009).
  R. V. Krems, *Molecules in electromagnetic fields: from ultracold physics to controlled chemistry* (2019).
- **Rotational** degrees of freedom are the most relevant at **ultracold temperatures**.
- But **hyperfine structure** can also be important.



Schematic diagram of the hierarchical structure of molecular energy levels.

Molecular rotation

- The **control** of molecular rotation has attracted significant attention in the past few years.
  C. P. Koch, M. Lemeshko, and D. Sugny, Rev. Mod. Phys. **91**, 035005 (2019).

- Due to the polar nature of most molecules, **rotational states can be controlled** with electromagnetic fields.

- Naturally, molecular rotation could be important in **molecular dipolar gases.**

- However, only a few works on interacting ultracold molecules have considered rotation.
  A. Micheli, G. Pupillo, H. P. Büchler, and P. Zoller, Phys. Rev. A **76**, 043604 (2007).
  M. L. Wall and L. D. Carr, New J. Phys. **11**, 055027 (2009).
  A. Dawid, M. Lewenstein, and M. Tomza, Phys. Rev. A **97**, 063618 (2018).

Free rotation of a molecule

- Classically, a molecule can be modelled as a **rigid rotor**

$$H_{\text{rot}} = \frac{\boldsymbol{J}_a^2}{2I_a} + \frac{\boldsymbol{J}_b^2}{2I_b} + \frac{\boldsymbol{J}_c^2}{2I_c}\,.$$

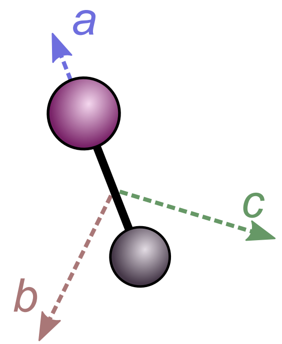
$$I_a \geq I_b \geq I_c$$

J_x: Angular momentum
I_x: Principal moments of inertia.

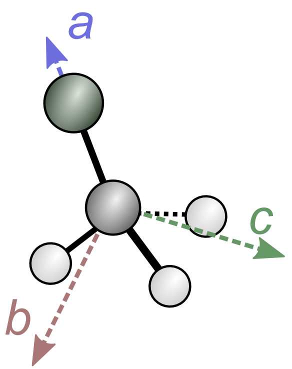
R. N. Zare, *Angular momentum: understanding spatial aspects in chemistry and physics* (1988).

- Molecules can be classified as:

$I_a = 0,\ I_b = I_c > 0$: Linear top
$I_a = I_b = I_c$: Spherical top
$I_a = I_b < I_c$: Oblate symmetric top
$I_a < I_b = I_c$: Prolate symmetric top
$I_a < I_b < I_c$: Asymmetric top



RbCs, a **linear diatomic** molecule.



CH_3F, a **prolate symmetric** top.

- **Centrifugal forces** can be considered with additional terms in the Hamiltonian.

Free rotation of a molecule

- **Quantum** rotation is described by the Hamiltonian

$$\hat{H}_{\mathrm{rot}} = A\hat{\boldsymbol{J}}_a^2 + B\hat{\boldsymbol{J}}_b^2 + C\hat{\boldsymbol{J}}_c^2\,, \qquad A \leq B \leq C$$

  where $A = \hbar/(4\pi I_a)$, $B = \hbar/(4\pi I_b)$, and $C = \hbar/(4\pi I_c)$ are the **rotational constants**.

- To diagonalise *H*, one uses the **symmetric top wavefunctions**

$$|j\,k\,m\rangle\,. \qquad j=0,1,\ldots\,,\ -j\leq k\leq j,\ -j\leq m\leq j$$

Free rotation of a molecule

- The $|j\,k\,m\rangle$ states diagonalise the angular momentum as

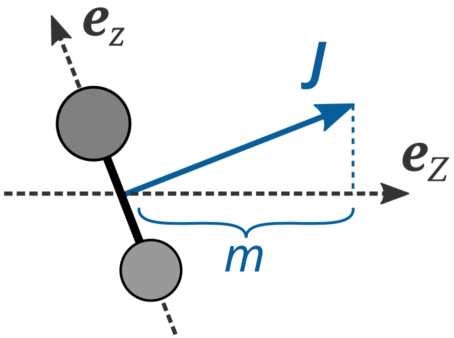
$$\hat{\boldsymbol{J}}^2\,|j\,k\,m\rangle = j(j+1)\,|j\,k\,m\rangle\,,$$

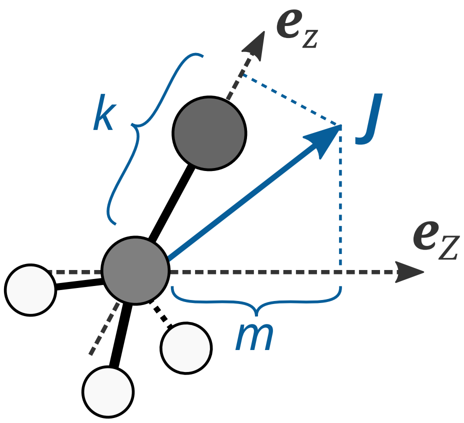
$$\hat{J}_z\,|j\,k\,m\rangle = k\,|j\,k\,m\rangle\,,$$

$$\hat{J}_Z\,|j\,k\,m\rangle = m\,|j\,k\,m\rangle\,.$$

Laboratory-fixed frame: (X, Y, Z)

Molecule-fixed frame: $(x, y, z) = (a, b, c)$: oblate symmetric tops
$(x, y, z) = (b, c, a)$: otherwise





Free rotation of a molecule

- **Linear top**: $A = 0,\, B = C \quad \longrightarrow \quad E_j = Bj(j+1)\,. \qquad k = 0$
- **Prolate tops**: $A > B = C \quad \longrightarrow \quad E_{j,k} = Cj(j+1) + (A - C)k^2\,.$
- **Oblate tops**: $A = B > C \quad \longrightarrow \quad E_{j,k} = Aj(j+1) + (C - A)k^2\,.$

These molecules are all diagonal in $|j\,k\,m\rangle$, and thus $(\boldsymbol{j\,k\,m})$ **are good quantum numbers**.

Free rotation of a molecule

- **Asymmetric tops**: $A > B > C$

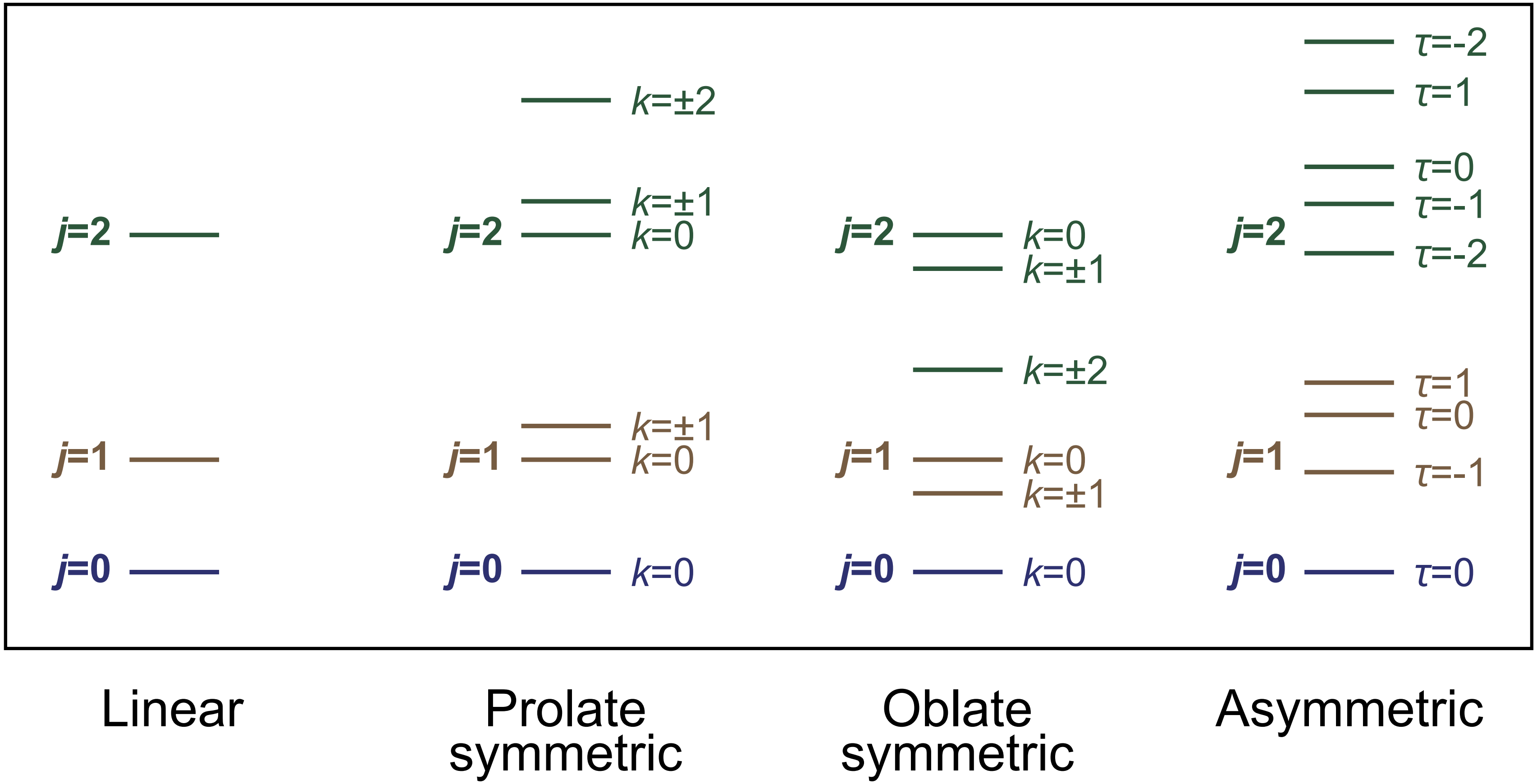
$$\langle j\,k\,m|\hat{H}_{\mathrm{rot}}|j\,k\,m\rangle = \frac{B+C}{2}\left(j(j+1)-k^2\right) + A\,k^2\,,$$

$$\langle j\,k\,m|\hat{H}_{\mathrm{rot}}|j\,k\pm 2\,m\rangle = \frac{B-C}{4} f_{\pm}(j,k)\,,$$

where $f_{\pm}(j,k) = \sqrt{[j(j+1)-k(k\pm 1)]\,[j(j+1)-(k\pm 1)(k\pm 2)]}$.

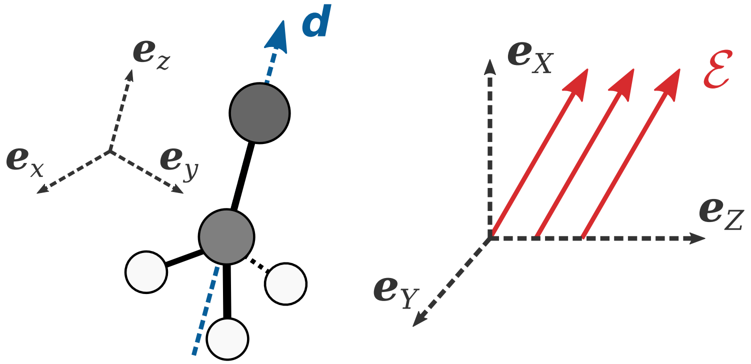
- *k* is **not a good quantum number**.
- One can define a pseudo-quantum number ***τ*** to label the eigenstates.

Free rotation of a molecule



Rotating molecule under a dc electric field

- A **rotating polar** molecule interacting with an external dc electric field $\mathcal{E}$:

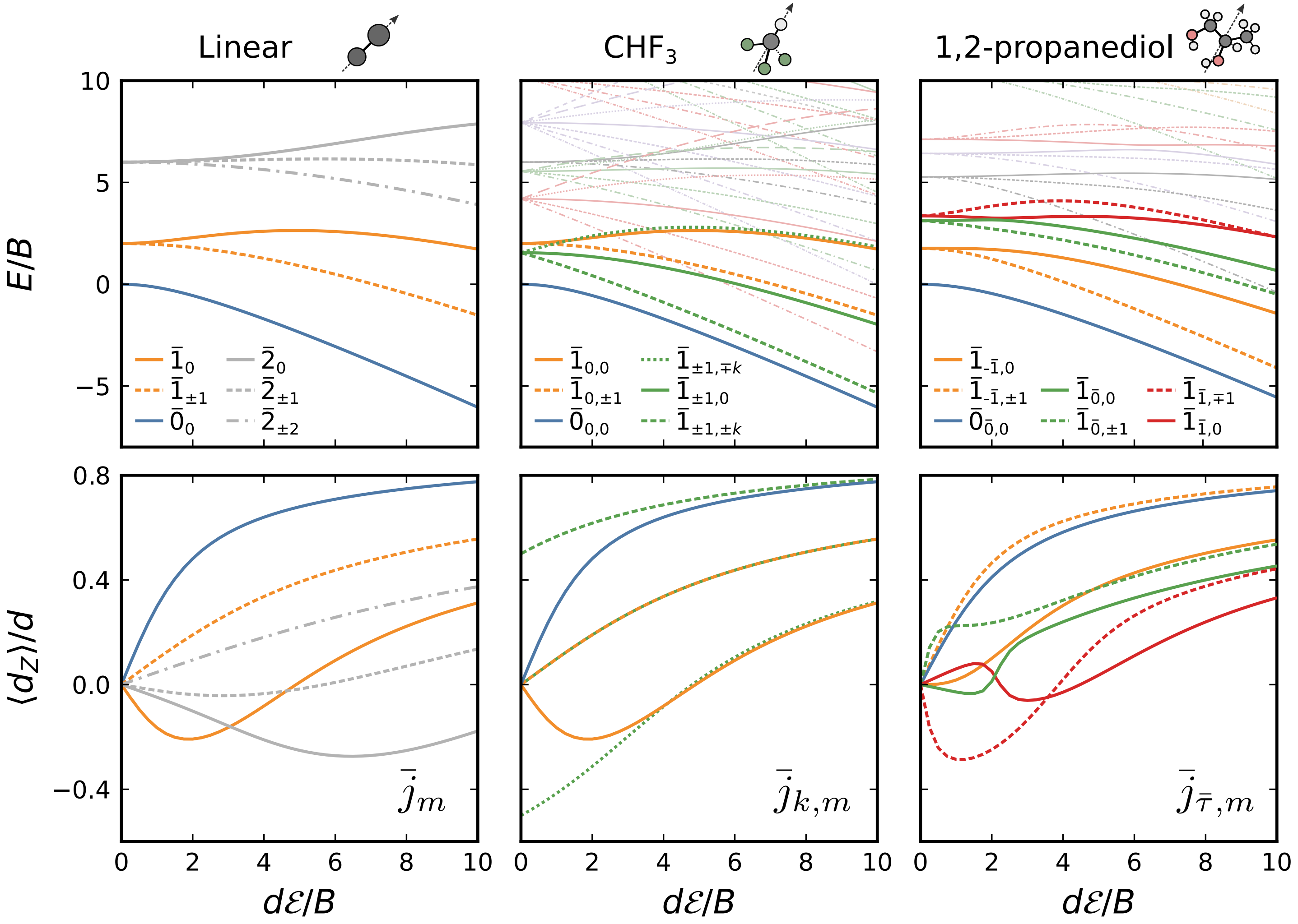


$$\hat{H} = \hat{H}_{\mathrm{rot}} - \hat{\boldsymbol{d}} \cdot \boldsymbol{\mathcal{E}} \,.$$

* Induced dipole moment can be considered with additional terms.

- To diagonalise the Hamiltonian one works with the $|j\ k\ m\rangle$ basis.
- The $|j\ k\ m\rangle$ states enable us to perform transformation between the molecule- and laboratory-fixed frames: **spherical tensors**.

Rotating molecule under a dc electric field



CHF$_3$ (oblate): A=B=10.348 GHz, C=5.6734 GHz, d_c=1.645 D.

1,2-propanediol (asymmetric) : A=8.57205 GHz, B=3.640 GHz, C=2.790 GHz, d_a=1.2 D, d_b=1.9 D, d_c=0.36 D.

Outline

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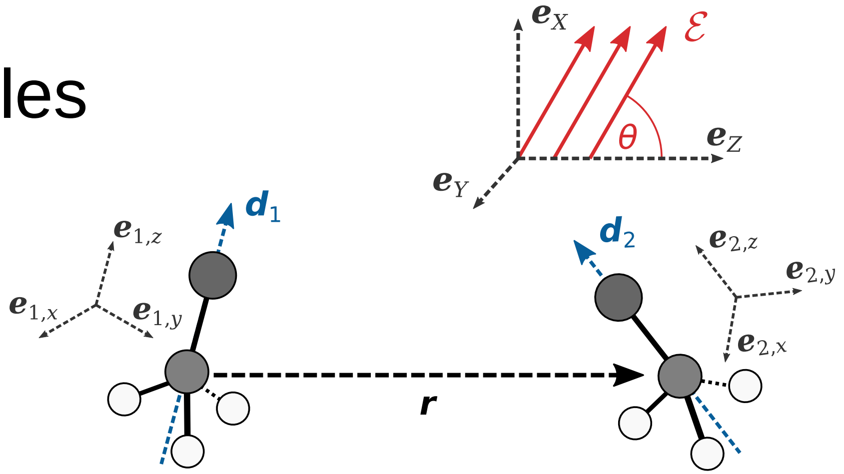
Two interacting polar molecules

- We consider two *static* polar molecules under an external dc electric field



$$\hat{H} = \hat{H}_{\mathrm{rot}} + \hat{H}_{\mathrm{dc}} + \hat{H}_{\mathrm{dd}} \,.$$

- **Rotation**:

$$\hat{H}_{\mathrm{rot}} = \sum_{i=1}^{2} \left(A\hat{\boldsymbol{J}}_{i,a_i}^2 + B\hat{\boldsymbol{J}}_{i,b_i}^2 + C\hat{\boldsymbol{J}}_{i,c_i}^2 \right) \,.$$

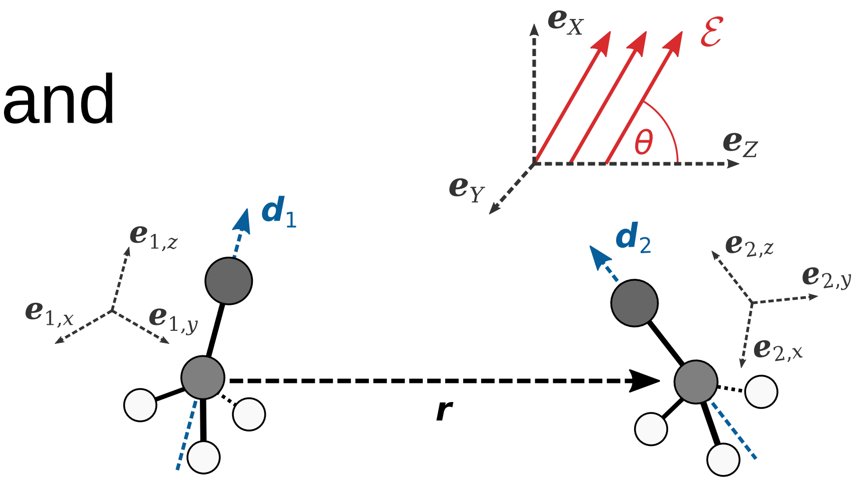
- **dc field**:

$$\hat{H}_{\mathrm{dc}} = -\sum_{i=1}^{2} \hat{\boldsymbol{d}}_i \cdot \boldsymbol{\mathcal{E}} \,.$$

- **dipole-dipole**:

$$\hat{H}_{\mathrm{dd}} = \frac{(\hat{\boldsymbol{d}}_1 \cdot \hat{\boldsymbol{d}}_2) - 3(\hat{\boldsymbol{d}}_1 \cdot \boldsymbol{e}_{\boldsymbol{r}})(\hat{\boldsymbol{d}}_2 \cdot \boldsymbol{e}_{\boldsymbol{r}})}{r^3} \,.$$

Two interacting polar molecules



- We examine the **energy spectrum** and **dipole polarisation**.

$$\langle d_L \rangle = \langle d_{1,L} + d_{2,L} \rangle / 2 \, . \quad L = X, Y, Z.$$

- We diagonalise the Hamiltonian **numerically** with a basis set

$$\alpha \equiv |j_1 \, k_1 \, m_1, j_2 \, k_2 \, m_2\rangle \, .$$

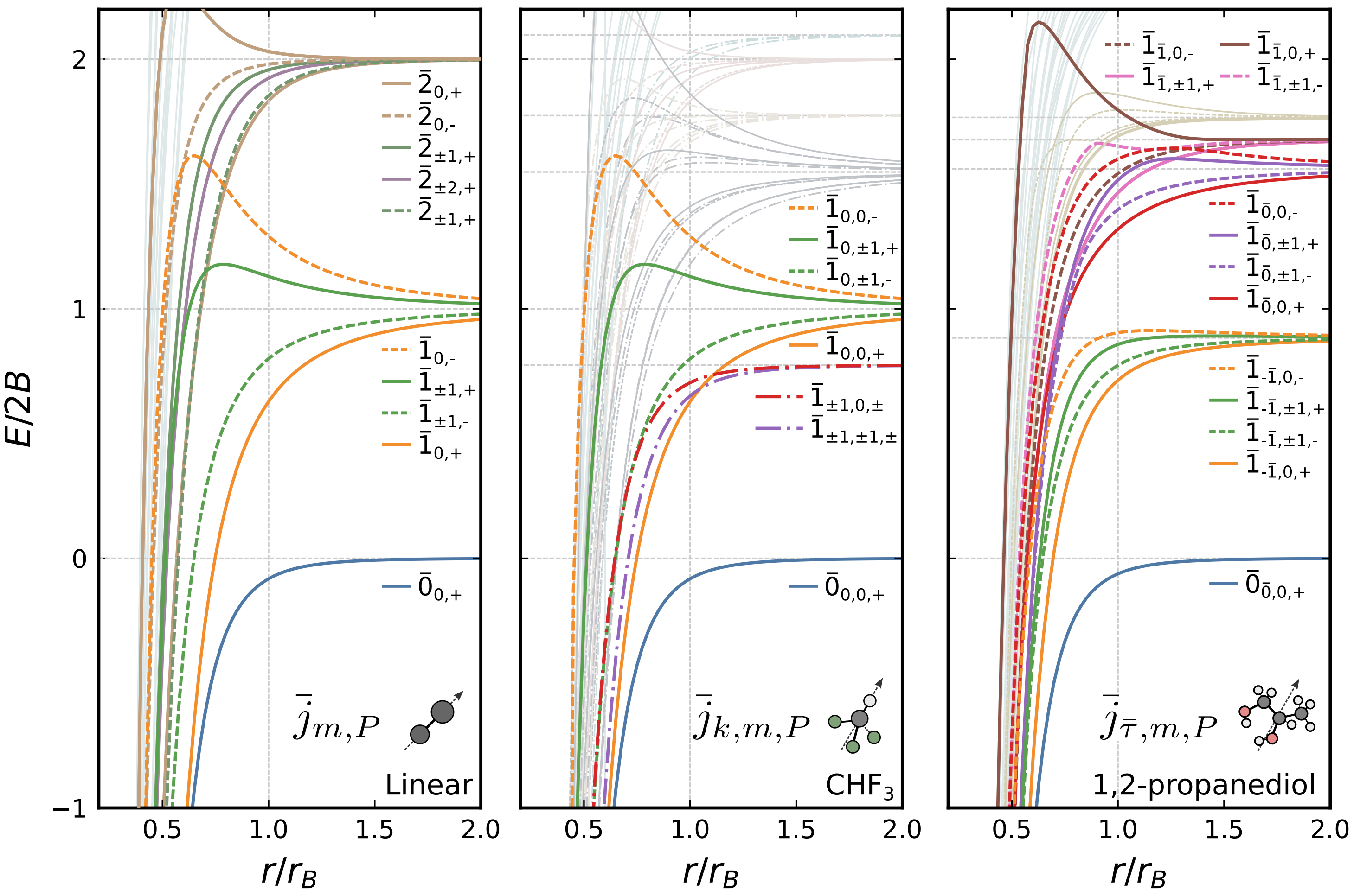
- We consider three molecules:
  - Linear
  - Fluoroform (CHF_3) : Oblate symmetric top

CHF_3 (oblate): A=B=10.348 GHz, C=5.6734 GHz, d_c=1.645 D.

  - 1,2-propanediol ($CH_3CHOHCH_2OH$) : Asymmetric top

A=8.57205 GHz, B=3.640 GHz, C=2.790 GHz, d_a=1.2 D, d_b=1.9 D, d_c=0.36 D.

Energy spectrum with no external field

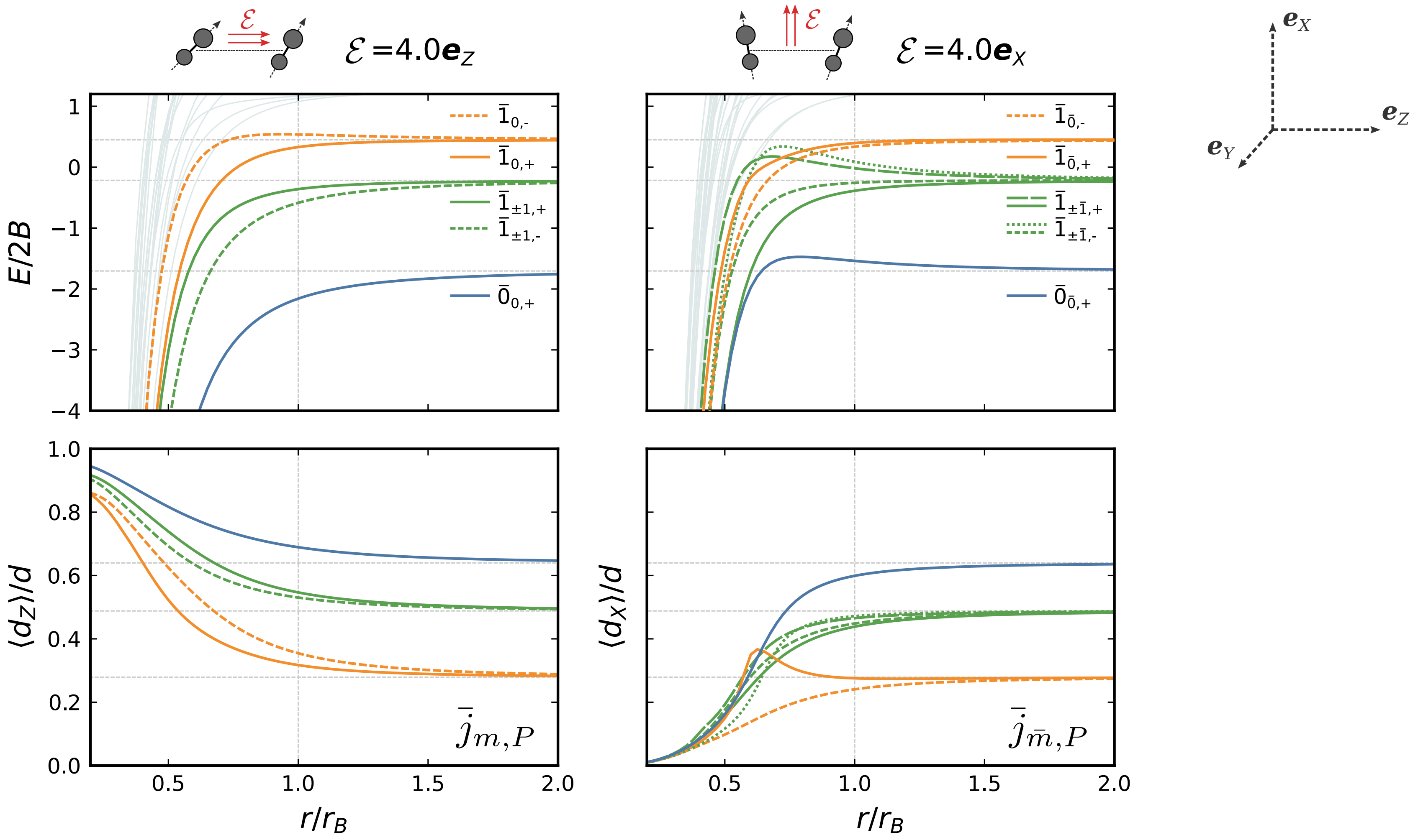


$$r_B = \left(d^2/B\right)^{1/3}$$

- The dipole-dipole interaction induces a rich spectrum.
- *m* is always conserved. *k* is conserved for symmetric tops.

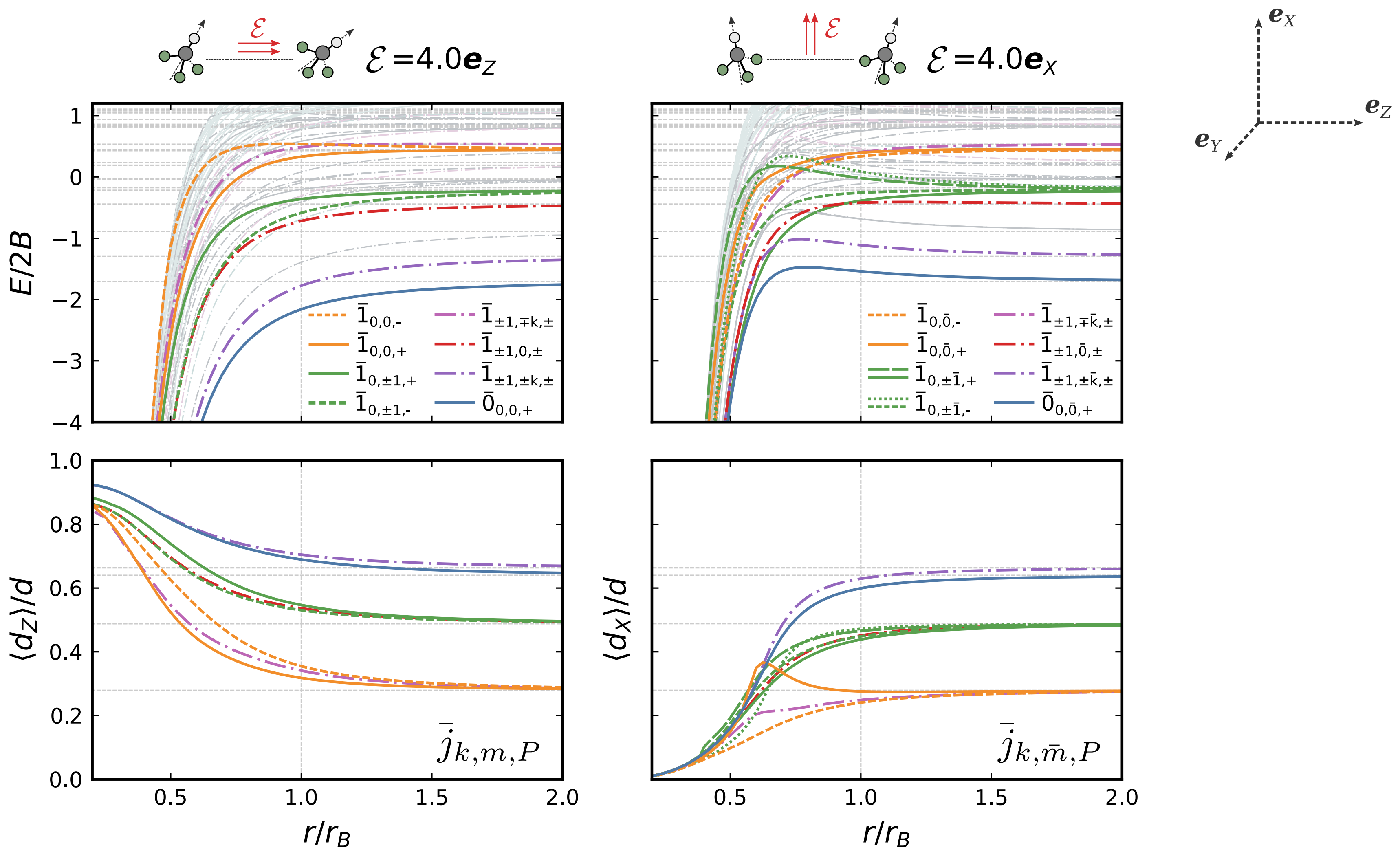
$$j = j_1 + j_2 \qquad m = m_1 + m_2, \qquad k = k_1 + k_2, \qquad P = +(\text{symmetric}), -(\text{antisymmetric})$$

Two linear molecules under a dc field



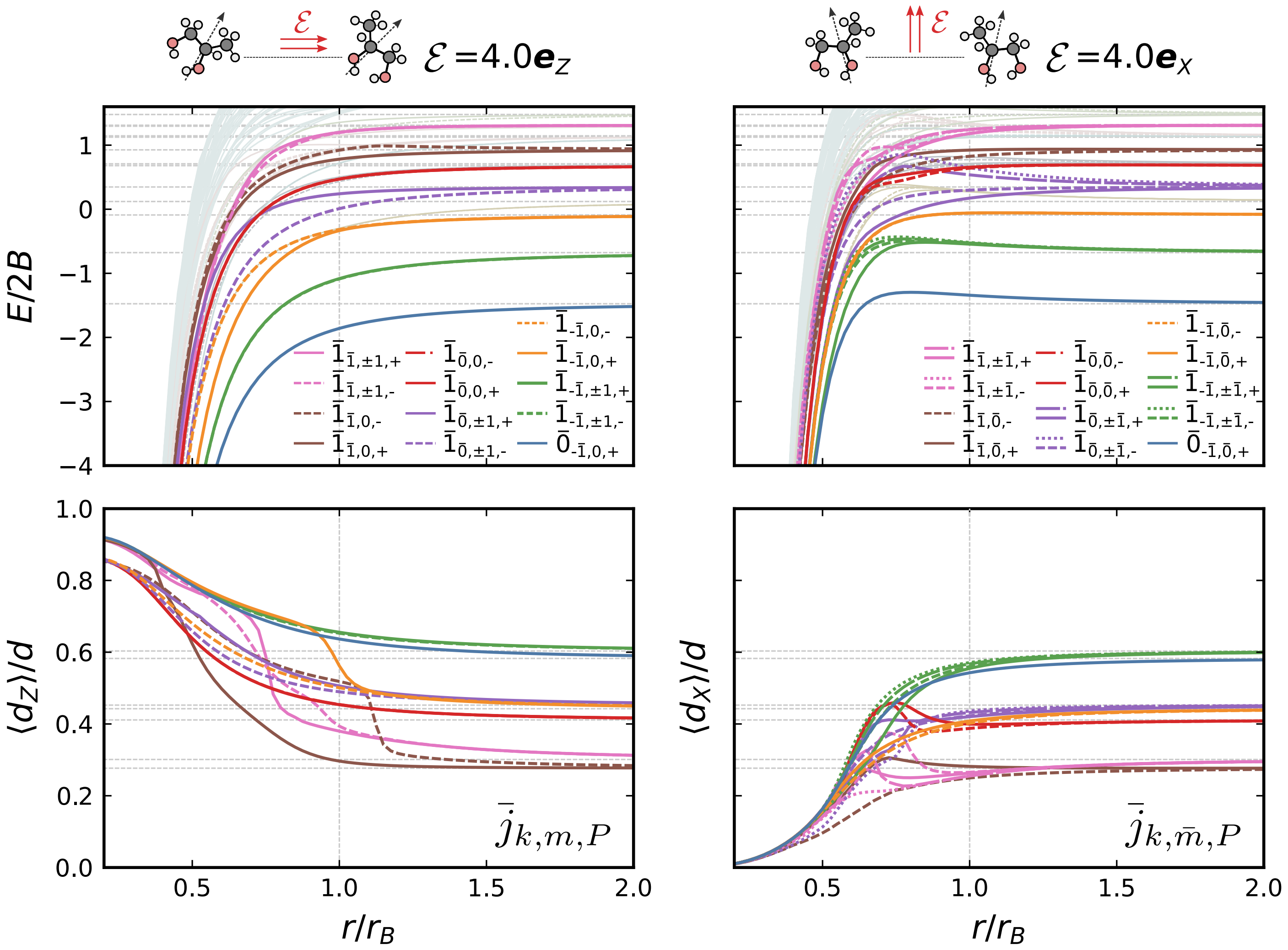
- The polarisation of the dipole moments depends strongly on the direction of the fields at short separations.
- *m* is only conserved for fields in the direction of ***r***.

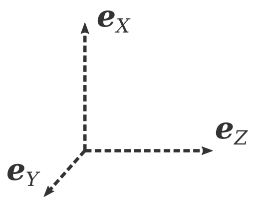
Two CHE$_3$ molecules under a dc field



- *m* is only conserved for fields in the direction of ***r***, but *k* is always conserved.

Two 1,2-propanediol molecules under a dc field





Conclusions

- We performed a comprehensive study of two interacting polar molecules under an external dc electric field.
- The energy spectrum and dipoles polarisation **depend strongly on the direction** of the external field.
- These effects should be considered in **quantum computing** and **ultracold molecular gases** applications.
- Future work:
    - Consider additional effects: **hyperfine structure**, centrifugal forces, **ac fields**, magnetic fields.
    - Perform **many-body calculations** of gases of ultracold polar and rotating molecules.

More details: **arXiv:2303.02199**

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Thank you!

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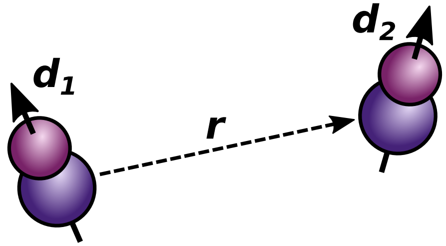
Dipole-dipole interaction

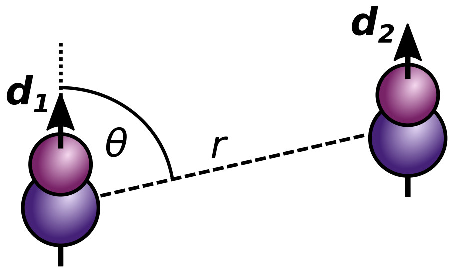
- The interaction between dipoles is **long-range** and **anisotropic**

$$V_{\mathrm{dd}} = \frac{(\boldsymbol{d}_1 \cdot \boldsymbol{d}_2) r^2 - 3(\boldsymbol{d}_1 \cdot \boldsymbol{r})(\boldsymbol{d}_2 \cdot \boldsymbol{r})}{r^5} \, .$$



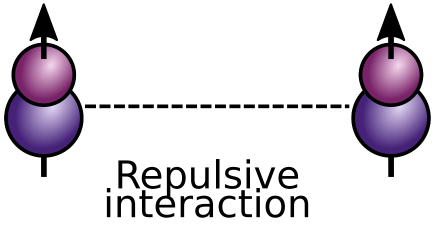
- If the dipoles are **polarised in the same direction**, it takes the simple form

$$V_{\mathrm{dd}} = \frac{1 - 3\cos\theta}{r^3} d^2 \, .$$



- The dipolar interaction produces rich physics, such as **crystalline** and **droplet** phases.

Lahaye *et al.*, Rep. Prog. Phys. **72**, 126401 (2009).



- It could also be exploited in quantum computing platforms.

K.-K. Ni, T. Rosenband, and D. D. Grimes, Chem Sci. **9**, 6830 (2018).

Molecular rotation

- The **control** of molecular rotation has attracted significant attention in the past few years.
  C. P. Koch, M. Lemeshko, and D. Sugny, Rev. Mod. Phys. **91**, 035005 (2019).

- Due to the polar nature of most molecules, **rotational states can be controlled** with electromagnetic fields.

- The control of rotational states has many potential applications:

  - Enantio-discrimination of chiral molecules.
    I. Tutunnikov, E. Gershnabel, S. Gold, and I. S. Averbukh, J. Phys. Chem. Lett. **9**, 1105 (2018).

  - **Quantum computing** platforms.
    K.-K. Ni, T. Rosenband, and D. D. Grimes, Chem Sci. **9**, 6830 (2018).
    P. Yu, L. W. Cheuk, I. Kozyryev, and J. M. Doyle, New J. Phys. **21**, 093049 (2019).
    P. D. Gregory, J. A. Blackmore, S. L. Bromley, J. M. Hutson, and S. L. Cornish, Nat. Phys. **17**, 1149 (2021).

Free rotation of a molecule

- **Quantum** rotation is described by the Hamiltonian

$$\hat{H}_{\text{rot}} = A\hat{\boldsymbol{J}}_a^2 + B\hat{\boldsymbol{J}}_b^2 + C\hat{\boldsymbol{J}}_c^2\,, \qquad A \le B \le C$$

where $A = \hbar/(4\pi I_a)$, $B = \hbar/(4\pi I_b)$, and $C = \hbar/(4\pi I_c)$ are the **rotational constants**.

- To diagonalise H, one uses the **symmetric top wavefunctions**

$$|j\,k\,m\rangle\,.$$

j=0,1,… , -*j*≤*k*≤*j*, -*j*≤*m*≤*j*

- These are defined as

$$\langle\Omega|j\,k\,m\rangle = \sqrt{\frac{2j+1}{8\pi}}\,D^{j*}_{m,k}(\Omega)\,.$$

Ω=(*ϕ*,*θ*,*χ*): Euler angles
D: Wigner *D*-matrices

- They are related to the spherical harmonics

$$D^{j}_{m,0}(\phi,\theta,\chi) = \left(\frac{4\pi}{2j+1}\right)^{1/2} Y^{*}_{j,m}(\theta,\phi)$$

Free rotation of a molecule

- **Linear top**: $A = 0,\ B = C$

$$\hat{H}_{\mathrm{rot}} = B\hat{\boldsymbol{J}}^2 \longrightarrow E_j = Bj(j+1)\,. \qquad\qquad k = 0$$

- **Prolate symmetric tops**: $A > B = C$

$$\hat{H}_{\mathrm{rot}} = C\hat{\boldsymbol{J}}^2 + (A - C)\hat{\boldsymbol{J}}_z^2 \longrightarrow E_j = Cj(j+1) + (A - C)k^2\,.$$

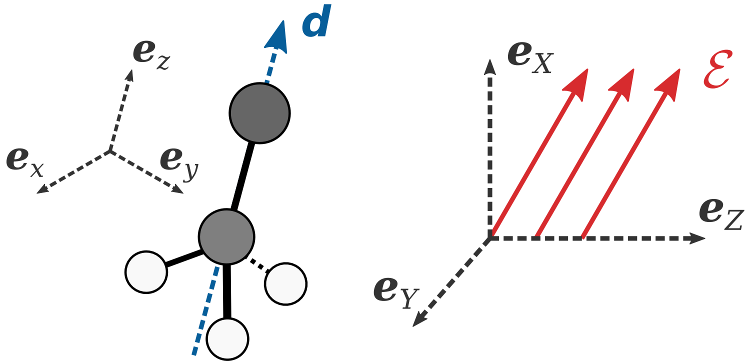
- **Oblate symmetric tops**: $A = B > C$

$$\hat{H}_{\mathrm{rot}} = A\hat{\boldsymbol{J}}^2 + (C - A)\hat{\boldsymbol{J}}_z^2 \longrightarrow E_j = Aj(j+1) + (C - A)k^2\,.$$

These molecules are all diagonal in $|j\,k\,m\rangle$, and thus ($\boldsymbol{j\,k\,m}$) **are good quantum numbers**.

Rotating molecule under a dc electric field

- A **rotating polar** molecule interacting with an external dc electric field $\mathcal{E}$:



$$\hat{H} = \hat{H}_{\text{rot}} - \hat{\boldsymbol{d}} \cdot \boldsymbol{\mathcal{E}} \,.$$

* Induced dipole moment can be considered with additional terms.

- To diagonalise the Hamiltonian one works with the $|j\ k\ m\rangle$ basis.
- The $|j\ k\ m\rangle$ states enable us to perform transformation between the molecule- and laboratory-fixed frames: **spherical tensors**.

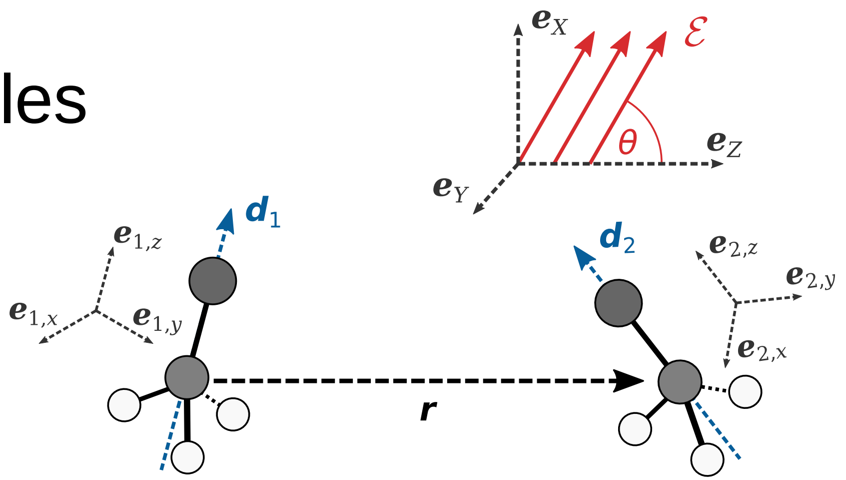
$$\hat{H}_{\text{dc}} = -\hat{\boldsymbol{d}} \cdot \boldsymbol{\mathcal{E}} = -\sum_{q,p} (-1)^p D^{1*}_{p,q}(\Omega) d_q \mathcal{E}_{-p} \,.$$

p,*q*=-1,0,1
p : laboratory-fixed frame
q : molecule-fixed frame

$$\boldsymbol{v}\ : \qquad v_0 = v_{z'}\,, \qquad v_{\pm 1} = \mp(v_{x'} \pm i\, v_{y'})/\sqrt{2}\,.$$

R. N. Zare, *Angular momentum: understanding spatial aspects in chemistry and physics* (1988).

Two interacting polar molecules



- We consider two *static* polar molecules under an external dc electric field

$$\hat{H} = \hat{H}_{\mathrm{rot}} + \hat{H}_{\mathrm{dc}} + \hat{H}_{\mathrm{dd}} \, .$$

- **Rotation**:

$$\hat{H}_{\mathrm{rot}} = \sum_{i=1}^{2} \left(A\hat{\boldsymbol{J}}_{i,a_i}^2 + B\hat{\boldsymbol{J}}_{i,b_i}^2 + C\hat{\boldsymbol{J}}_{i,c_i}^2 \right) \, .$$

- **dc field**:

$$\hat{H}_{\mathrm{dc}} = -\sum_{i=1}^{2} \hat{\boldsymbol{d}}_i \cdot \boldsymbol{\mathcal{E}} \, .$$

- **dipole-dipole**:

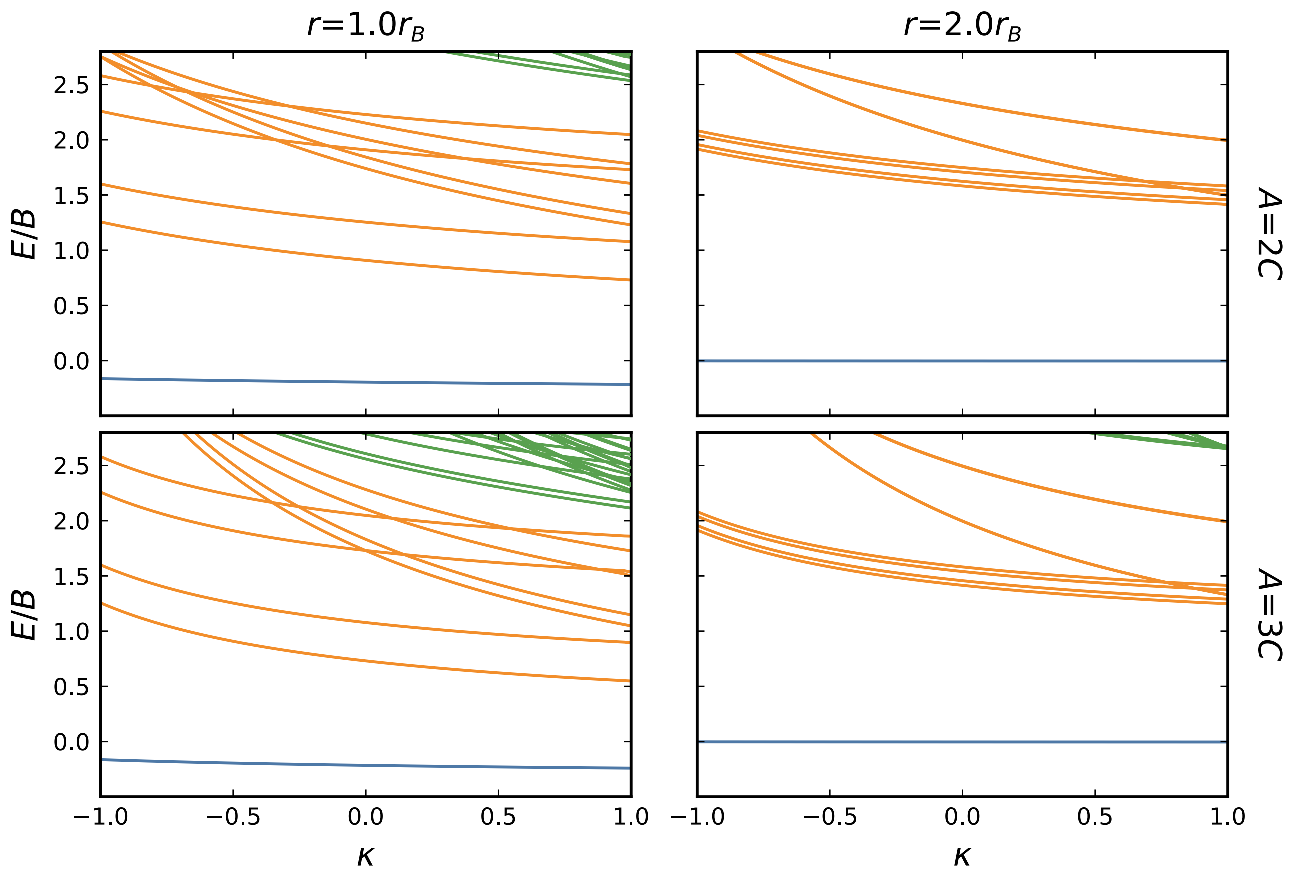
$$\hat{H}_{\mathrm{dd}} = \frac{(\hat{\boldsymbol{d}}_1 \cdot \hat{\boldsymbol{d}}_2) - 3(\hat{\boldsymbol{d}}_1 \cdot \boldsymbol{e}_{\boldsymbol{r}})(\hat{\boldsymbol{d}}_2 \cdot \boldsymbol{e}_{\boldsymbol{r}})}{r^3} \, ,$$

which can be written as

$$\hat{H}_{\mathrm{dd}} = -\frac{\sqrt{6}}{r^3} \sum_{p=-2}^{2} (-1)^p C_{-p}^{(2)}(\Omega_r) [\hat{\boldsymbol{d}}_1 \otimes \hat{\boldsymbol{d}}_2]_p^{(2)} \, .$$

$C_m^{(l)}$: unnormalised spherical harmonic

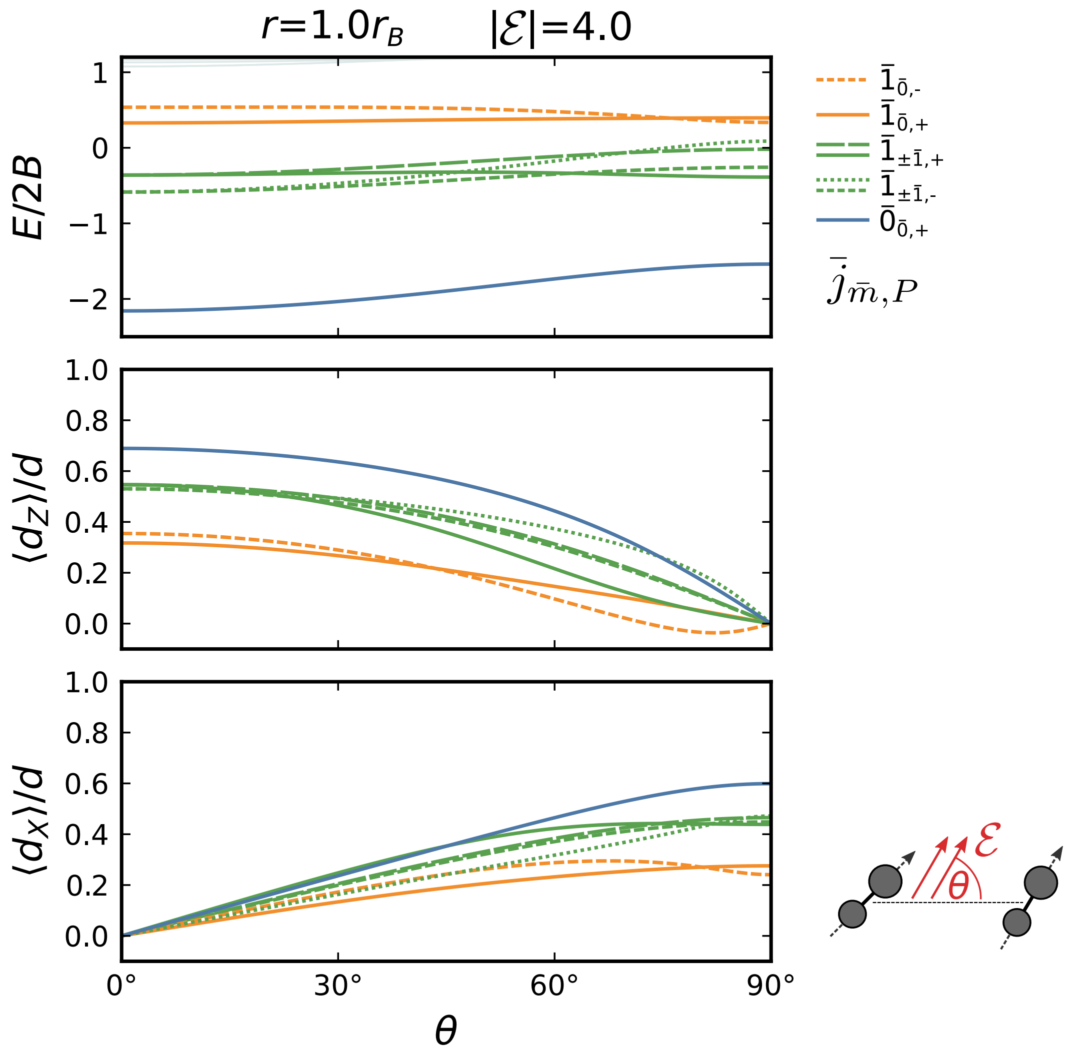
Energy spectrum with no external field

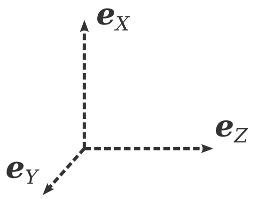


$$\kappa = \frac{2B - A - C}{A - C}$$

- The energy levels depend on the **separation** and **rotational constants**.
- This could be used to experimentally measure the moments of inertia (optical tweezers?).

Two linear molecules under a dc field





- *m* is only conserved for *θ*=0.
- The dc field and the dipolar interaction **compete** to polarise the molecules.