Molecular Quantum Degrees of Freedom

- Energy
- Internuclear Separation
- electronic transitions
- vibrational levels ($v$)
- rotational levels ($J$)
- hyperfine levels
Molecular Quantum Degrees of Freedom

Energy

Internuclear Separation

v, vibrational levels

J, rotational levels

electronic transitions

hyperfine levels


https://experiencetalk.files.wordpress.com/2014/04/corn-mri-scan.gif
First “Atomic” Clock, 1949

Clock Regulated by Vibrations of Molecules Keeps Perfect Time

So accurate that it will lose only one second in 300 years, an atomic clock developed at the Bureau of Standards is controlled by the constant, natural vibration of atoms in the ammonia molecule. The atomic timepiece is the first clock not dependent on astronomical observation.

Driven by a quartz-crystal oscillator, the clock is a complex electronic instrument. A low-frequency radio signal, generated by the crystal oscillator, is transformed into a very high frequency signal. This signal is then compared with the natural vibration frequency of the ammonia molecule, which oscillates or turns itself inside-out 24 billion times a second. When the two frequencies differ, an “error signal” adjusts the oscillator, bringing them into agreement. The natural frequency of the ammonia molecule being invariable, this continuous synchronization enables the clock to tick off seconds far more accurately than any other method.
“Ticking” of atomic clock

\[ S = \frac{Al^+/Hg^+/Sr/Yb}{\omega = \sim 2\pi \times 10^{15} \text{ Hz}} \]
Quantum Control of Molecules

- cooling and trapping
- long interaction and probe time
- building complex system from the bottom up

Why Ultracold Molecules?

- search for new physics
- exotic quantum matter
- quantum computing
- ultracold chemistry
### Fundamental Physics with Molecules

#### “Nature’s high E-field laboratory”
- Searches for EDMs and other symmetry violations
- Bond distorts atomic orbitals (enhanced sensitivities)
- Molecular symmetries cancel systematics (co-magnetometer)

#### Bonded nuclei as “test masses”
- Testing gravity at nanometer scales
- Ultracold Sr$_2$ – T. Zelevinsky, Columbia U

#### Testing precision theory
- High precision spectroscopy benchmarks theory
- CaH$^+$, NIST ion storage group
Fundamental Chemistry with Cold Molecules

probing potential energy surfaces beyond “gold-standard” quantum chemistry calculation

Narevicius (Weizmann)

van de Meerakker (Radboud)
Science 368, 626 (2020)

synthesizing new chemical species

Hudson (UCLA)
Science 357, 1370 (2017)

Direct detection of reaction intermediate


Other work: Ye, Denschlag, Zelevinsky, Willitsch, Zare, …
Outline (Lecture 1)

- Quantum computing/simulations with molecules (theoretical ideas)
- Preparing single ultracold polar molecules
- Assembling molecules from atoms

Laser-cooled molecules

CUA Doyle/Ketterle/Ni Collaboration
Science 365, 1156 (2019)
Yale, Imperial, JILA...

Assemble molecules from atoms

Science 360, 900 (2018)
Cairncross*, Zhang* et al., PRL 126, 123402 (2021)
Wuhan, Durham, JILA, MIT, Innsbruck
Hong Kong, MPQ, Hannover,...

Molecular ions

PTB, Basel, UCLA, UCSB,...
Outline (Lecture 2)

- Probing sub-microkelvin chemistry
(Designer) Ultracold Molecules for quantum simulation and computation

- larger variety of internal states for storage and interaction
- intrinsic molecular couplings between internal degrees of freedom

\[
\hat{H}_{DD} = \frac{1}{4\pi\varepsilon_0 r^3} \left[ \hat{d}_1 \cdot \hat{d}_2 - 3(\hat{d}_1 \cdot \hat{e}_r)(\hat{d}_2 \cdot \hat{e}_r) \right]
\]

DeMille, PRL 88, 067901 (2002), Yelin, others…
Ni group, Chemical Science 9, 6830-6838 (2018)
(Designer) Ultracold Molecules for quantum simulation and computation

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<th>Qubit 1</th>
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<tr>
<td>1</td>
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Dipole-dipole interaction

\[ \hat{H}_{DD} = \frac{1}{4\pi\varepsilon_0 r^3} \left[ \hat{d}_1 \cdot \hat{d}_2 - 3(\hat{d}_1 \cdot \hat{e}_r)(\hat{d}_2 \cdot \hat{e}_r) \right] \]

1. Prepare a 50/50 superposition of \(|0\rangle\text{ and } |e\rangle\) [a global single-particle pi/2-pulse]
2. Wait for \(t=\pi/(2 \Omega)\)
3. Apply another global single-particle pi/2-pulse
4. Realize a Bell state \((|00\rangle + |ee\rangle)/2\)
Two-Qubit (iSWAP) Gates (scheme)

- Avoid DC electric-field or dressed field

All states are field insensitive & long-lived
Exchange occurs at zero external E-fields

(Ni group) Chemical Science 9, 6830-6838 (2018)
Hudson & Campbell, PRA 98, 040302 (2018)
motivated by Theoretical work: Demler, Lukin, Rey, Gorshkov; Exp work: Jin/Ye, Zwierlein
The full picture

* molecule of choice: NaCs
* exchange time of 50 μs, for F>99.6% @ B-field = 35G (limited by off-resonance excitations)
* exchange time of ~3ms (gate time~10ms), F>99.99% @ B-field = 1 G

Ni, Rosenband, Grimes, Chemical Science 9, 6830-6838 (2018)
building single molecules

in the rovibrational ground state
and the motional ground state

Laser-cooled molecules

CUA Doyle/Ketterle/Ni Collaboration

Anderegg et al., Science 365, 1156 (2019)

Other work: Molecular ions

Assembly molecules from atoms

(Ni Group) Science 360, 900 (2018)

related work: Wuhan group
Two approaches

**a** Loading single molecules from an ensemble

- Load
- Purify Internal state
- Motional sideband cooling

**b** Building single molecules from single atoms

- Trap & cool
- Merge
- Molecule association
- Internal state transfer
Building Single Molecules

**Na+Cs → NaCs**

**References**

ChemistryViews

Science 360, 900 (2018)


Associate Molecules from Ultracold Atoms

Main challenge: efficient molecule creation while staying cold

- Inter-particle spacing $R$
- Wavefunction overlap $\sim 10^{-6}\%$
- Energy $E$
- Inter-particle spacing $R$ $\rightarrow$ 6000 K
- 1K = 0.002 kCal/mol $\sim$ 1 cm$^{-1}$

0.2 nm

50 nm
Associate Molecules from Ultracold Atoms

Two-step solution:

**Step 1:** bind atoms into weakly bound molecules through a Fano-Feshbach resonance, “Feshbach molecules” (this prepares them in a single quantum state)

**Step 2:** two-photon coherent transfer to ro-vibrational ground state. Stimulated photon takes away excess binding energy

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Innsbruck and JILA (2008)
Durham, MIT, Hong Kong, MPQ, USTC, Harvard, Hannover
Atom state preparation

Cs

Na

Raman sideband cooling

Cs: 96%, Na: 93.5%

Single motional state!

PRA 97, 063423 (2018)

PRX 9, 021039 (2019)
Collisions of two atoms

- no reactions
  (because needs to simultaneous fulfill conservations of energy and momentum)
- To make a molecule, additional stimulated fields (light or magnetic) will need to be added
Turning a two-body problem to an one-body problem

To center of mass and relative coordinates

\[ H = \sum_{i=x,y,z} \left( \frac{m_1 \omega^2_{1,i} x^2_{1,i}}{2} + \frac{p^2_{1,i}}{2m_1} \right) + \sum_{i=x,y,z} \left( \frac{m_2 \omega^2_{2,i} x^2_{2,i}}{2} + \frac{p^2_{2,i}}{2m_2} \right) + V_{\text{int}}(\vec{r}_1 - \vec{r}_2) \]

Center of mass

\[ M = m_1 + m_2 \]
\[ \Omega^2_i = \frac{m_1 \omega^2_{1,i} + m_2 \omega^2_{2,i}}{m_1 + m_2} \]
\[ x_i = \frac{m_1 x_{1,i} + m_2 x_{2,i}}{m_1 + m_2} \]
\[ p_i = p_{1,i} + p_{2,i} \]

Relative

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]
\[ \omega^2_{R,i} = \frac{m_2 \omega^2_{1,i} + m_1 \omega^2_{2,i}}{m_1 + m_2} \]
\[ x_{R,i} = x_{1,i} - x_{2,i} \]
\[ p_{R,i} = \frac{m_2 p_{1,i} - m_1 p_{2,i}}{m_1 + m_2} \]

Mixing

\[ H = \sum_{i=x,y,z} \left( \frac{M \Omega^2_i x_i^2}{2} + \frac{P_i^2}{2M} \right) + \sum_{i=x,y,z} \left( \frac{\mu \omega^2_{R,i} x_{R,i}^2}{2} + \frac{P^2_{R,i}}{2\mu} \right) + V_{\text{int}}(\vec{r}_R) + \sum_{i=x,y,z} \mu (\omega^1_{1,i} - \omega^2_{2,i}) X_i x_{R,i} \]
Ramp Through a Fano-Feshbach Resonance

(a) 
bound state in "closed" channel

Energy

R

Energy

(b) 
"closed"
"open"

molecule

B field ramp

atoms

Energy
Feshbach Molecule Creation Efficiency

Most important parameters: PSD

For heteronuclear species, competing factors including cloud overlap and 3-body loss

Efficiency $\sim 15\%$

Hodby..Regal..Greiner..Jin..Cornell…Wieman, PRL 94, 120402 (2005)

Weakly-bound molecule formation

Absolute ground state atoms \( \rightarrow \) External + rotational ground state molecules
Mapping total control of atomic states to single molecules

Atom pair motional states

Magnetic association

Molecular states

S-wave Scattering resonance

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<th>External + rotational ground state molecules</th>
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External - rotational, vibrational
Mapping an Atom motional excitation to a Molecular Internal state excitation

P-wave molecules

\[ \Delta n = 1 \]

\[ \Gamma_{OP} \]

\[ \delta \]

\[ |3, -3; n\rangle \]

\[ |4, -4; n\rangle \]

\[ |4, -4; n-1\rangle \]

\[ \Omega_{F3} \]

\[ \Omega_{F4} \]
Molecular Internal and External state control

- Molecule conversion efficiency
  - Determined by relative motional ground state population of atom pair
  - ~45-50% (of initial loaded atoms)
  - Not fundamentally limited

- Molecular state purity
  - Internal state pure
  - External state determined by COM motional state population of atom pair
  - ~77% in ground state

\[
P(n_{\text{mol-com}} = 0) = \frac{P(n_{\text{rel}} = 0, n_{\text{com}} = 0)}{P(n_{\text{rel}} = 0)}
= 1 - \frac{m_{\text{Na}}}{M} \frac{\bar{n}_{\text{Na}}}{\bar{n}_{\text{Na}} + 1} - \frac{m_{\text{Cs}}}{M} \frac{\bar{n}_{\text{Cs}}}{\bar{n}_{\text{Cs}} + 1}.
\]

Zhang et al., PRL 124, 253401 (2020)
single NaCs molecules in the internal and motional ground state

Lifetime in excess of 3s
One molecular qubit is now fully controlled!

Next: Scaling up and entangle them

10 Na and 10 Cs atoms side-by-side

※ 3D ground-state cooling in 10 traps, nbar=0.06(22), 0.07(2), 0.05(2)