Probing weakly bound molecules with nonresonant light

Mikhail Lemeshko       Bretislav Friedrich

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DPG Jahrestagung
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Outline

1. Structure of weakly bound molecules
2. Molecules in nonresonant laser fields
3. What about experiments?
4. Probing weakly bound species by short laser pulses
5. Results for weakly bound $^{85}\text{Rb}_2$ molecules
6. Conclusions and outlook
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1. Structure of weakly bound molecules
2. Molecules in nonresonant laser fields
3. What about experiments?
4. Probing weakly bound species by short laser pulses
5. Results for weakly bound $^{85}$Rb$_2$ molecules
6. Conclusions and outlook
In molecular physics, most potentials have an asymptotic form $V(r) \sim -C_n/r^n$. 

- $n = 1$: Coulomb potential (H atom)
- $n = 2$: ion/electron + polar molecule
- $n = 3$: two polar molecules
- $n = 4$: ion/electron + atom
- $n = 6$: two atoms (molecular potential)
Molecular potentials

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What happens near the threshold?

Near-threshold states have large quantum numbers

We like to think that this justifies the semiclassical (WKB) approximation

$$V(r)$$

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Harald Friedrich and Johannes Trost, “Working with WKB waves far from the semiclassical limit”, Physics Reports 397, 359 (2004)

Mikhail Lemeshko (FHI)

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![Graph showing potential energy $V(r)$ versus distance $r$]
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But, for $V(r) \sim -C_n/r^n$ with $n > 2$
the region near threshold is anticlassical!

For molecules $n = 6$: WKB doesn’t work
for weakly bound vibrational states

Harald Friedrich and Johannes Trost, “Working with WKB waves far from the semiclassical limit”,
Physics Reports 397, 359 (2004)
Vibrational structure of weakly bound molecules

There were many attempts to describe vibrations of weakly bound molecules.

The first one: a classic paper by LeRoy and Bernstein:

Dissociation Energy and Long-Range Potential of Diatomic Molecules from Vibrational Spacings of Higher Levels*

Robert J. LeRoy and Richard B. Bernstein

Theoretical Chemistry Institute and Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706

(Received 12 December 1969)

An expression is derived which relates the distribution of vibrational levels near the dissociation limit \( D \) of a given diatomic species to the nature of the long-range interatomic potential, in the region where the latter may be approximated by \( D - C_n/R^n \). Fitting experimental energies directly to this relationship yields values of \( D, n, \) and \( C_n \). This procedure requires a knowledge of the relative energies and relative vibrational numbering for at least four rotationless levels lying near the dissociation limit. However, it requires no information on the rotational constants or on the number and energies of the deeply bound levels. \( D \) can be evaluated with a much smaller uncertainty than heretofore obtainable from Birge–Sponer extrapolations. The formula predicts the energies of all vibrational levels lying above the highest one measured, with uncertainties no larger than that of the binding energy of the highest level. The validity of the method is tested with model potentials, and its usefulness is demonstrated by application to the precise data of Douglas, Møller, and Stoicheff for the \( B^3\Pi_{0u}^+ \) state of Cl\(_2\).
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An expression is derived which relates the distribution of vibrational levels near the dissociation limit $D$ of a given diatomic species to the nature of the long-range interatomic potential, in the region where the latter may be approximated by $D - C_0/R^6$. Fitting experimental energies directly to this relationship yields values of $D$, $C_0$, and $C_0$. This procedure requires a knowledge of the densities of states and relative vibrational numbering near the dissociation limit, but it requires no information about the rotation, translation, or electronic states of the multiply bound levels. $D$ can be evaluated with a much smaller uncertainty than heretofore obtainable from Birge–Sponer extrapolations. The formula predicts the energies of all vibrational levels lying above the highest one measured, with uncertainties no larger than that of the binding energy of the highest level. The validity of the method is tested with model potentials, and its usefulness is demonstrated by application to the precise data of Douglas, Møller, and Stoicheff for the $B^3Π_{g,a}^+$ state of $Cl_2$. 

They used WKB.
There were many attempts to describe vibrations of weakly bound molecules. The first one: a classic paper by LeRoy and Bernstein:

They used WKB for their calculations. More or less good results for density of states $dv/dE_b$, but not for absolute values of $E_b$. Not applicable to really weakly bound molecules.
Structure of weakly bound molecules

Improvements to the LeRoy-Bernstein quantization rule

Stimulated by the cold-molecule research, many improvements have been proposed:

Eur. Phys. J. D 12, 199–209 (2000)

**Analytical correction to the WKB quantization condition for the highest levels in a molecular potential**

C. Boisseau¹, E. Audouard¹, J. Vigué¹,a, and V.V. Flambaum²

¹ Laboratoire Collisions Agrégats Réactivité, Université Paul Sabatier², 112 route de Narbonne, 31062 Toulouse Cedex, France
² School of Physics, University of New South Wales, Kensington, New South Wales 2033, Australia

**Improved LeRoy–Bernstein near-dissociation expansion formula, and prospect for photoassociation spectroscopy**

Daniel Comparat³

³ Laboratoire Aimé Cotton, CNRS II, Bât. 505, Campus d’Orsay, 91405 Orsay cedex, France

**Reexamination of the LeRoy-Bernstein formula for weakly bound molecules**

Haikel Jelassi, Bruno Viaris de Lesegno, and Laurence Pruvost

³ Laboratoire Aimé Cotton, CNRS II, Université Paris-Sud, Paris, France

Mikhail Lemeshko (FHI)

Probing weakly bound molecules
Patrick Raab and Harald Friedrich derived the so-called “quantization function”

\[ \text{Physical Review A 78, 022707 (2008)} \]

**Quantization function for deep potentials with attractive tails**

Patrick Raab and Harald Friedrich

*Physik Department, Technische Universität München, D-85747 Garching, Germany*

Their theory describes the vibrational structure of weakly bound molecules pretty well...

...but what does the “quantization function” mean?
The quantization function of Raab and Friedrich

We consider a state with vibrational quantum number $v$ and a binding energy $E_b$.
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The difference, $v_{th} - v$ depends in some way on the binding energy $E_b$:

$$v_{th} - v = F(E_b)$$

$F(E_b)$ is called the quantization function.
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The quantization function gives positions of weakly bound vibrational levels
The quantization function of Raab and Friedrich

The analytic expression for the quantization function is:

\[
F(E_b) = F_{th}(\kappa) + F_{ip}(\kappa) \left[ F_{cr}(\kappa) + F_{WKB}(\kappa) \right],
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where \( \kappa \sim \sqrt{E_b} \) is the wavevector.
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\[ F_{\text{WKB}}(\kappa) = \frac{\kappa^{1-2/n}}{\sqrt{\pi}(n-2)} \frac{\Gamma(\frac{1}{2} + \frac{1}{n})}{\Gamma(1 + \frac{1}{n})} \quad \text{— pure WKB term} \]
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\[ F_{th}(\kappa) = \frac{2b\kappa - (p\kappa)^2}{2\pi \left[ 1 + (G\kappa)^4 \right]} \] — near-threshold dependence
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The expressions are very accurate and can be used for any binding energy \( E_b \).
Now we know the vibrational structure. But what about rotation?
Rotational structure of weakly bound molecules

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Two years after introducing the quantization rule, LeRoy published an article:

**Canadian Journal of Physics**

*Published by The National Research Council of Canada*

**Dependence of the Diatomic Rotational Constant $B_v$ on the Long-Range Internuclear Potential**

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*Department of Physics, University of Toronto, Toronto 181, Ontario*
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The WKB approximation was depressingly inaccurate, as LeRoy pointed out:

As a result, only upper and lower bounds could be given, rather than accurate predicted values for unobserved $B_v$'s for levels near $D$. 
Rotational structure of weakly bound molecules: our contribution

We follow Raab and Friedrich to study rotation of weakly bound species

We consider a molecule in ground rotational state, $J = 0$, with a binding energy $E_b$

Rotation adds a centrifugal term to the potential,

$$V_{\text{cent}} = \frac{\hbar^2}{2} \frac{J(J+1)}{mr^2}$$

If the angular momentum $J$ is greater than some critical value $J^*$, the vibrational state is "pushed out" of the potential – the molecule dissociates.

$$r_{J=0} = \frac{E_b}{V(r)}$$

$r_{J=0}$ gives the number of rotational states, supported by a given vibrational level.
We follow Raab and Friedrich to study rotation of weakly bound species.

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If the angular momentum \( J \) is greater than some critical value \( J^* \), the vibrational state is “pushed out” of the potential – the molecule dissociates.

Integer part of \( J^* \) gives the number of rotational states, supported by a given vibrational level.
Rotational structure of weakly bound molecules: our contribution

- We derived a simple analytic expression for a number of rotational states supported by a weakly-bound molecule:

\[ J^* = F(E_b)(n - 2) \]

\( F(E_b) \) – the quantization function of Raab and Friedrich (you need \( C_6 \) and \( E_b \)),

\( n \) – power of the potential \( V(r) = -C_n/r^n \)
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- We derived a simple analytic expression for a number of rotational states supported by a weakly-bound molecule:

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- When the molecule is rotationless? We derived a simple criterion for that.
  
  Molecule has only the ground rotational state if the binding energy satisfies:

\[
E_b < d_6 \hbar^3 m^{-3/2} C_6^{-1/2} \quad \text{(for } n = 6)\]

- Rotational constants of weakly bound levels may be estimated as

\[
B = E_b J^*(J^* + 1)
\]
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\[ E_b < d_6 \hbar^3 m^{-3/2} C_6^{-1/2} \quad \text{(for } n = 6) \]

\( m \) is the reduced mass, \( d_6 \approx 1.6 \) is a parameter

• Rotational constants of weakly bound levels may be estimated as

\[ B = \frac{E_b}{J^*(J^* + 1)} \]
Rotational structure of weakly bound molecules: our contribution

These expressions are surprisingly accurate, see PRA 79 050501(R) (2009)

Last bound states of $^{85}$Rb$_2$:

\[
\begin{array}{ccc}
  v & J^* & J^*_\text{exact} \\
  123 & 0.22 & 0.22 \\
  122 & 4.25 & 4.25 \\
  121 & 8.28 & 8.48 \\
\end{array}
\]
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2. Molecules in nonresonant laser fields
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6. Conclusions and outlook
Is angular momentum always quantized?

In the absence of a field, \( \langle J^2 \rangle = J(J + 1) \) is an integer for states with \( J = 0, 1, 2 \ldots \)
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However, in the presence of a field, this is not true!

An external field, such as a laser field, hybridizes rotational levels, forming a “pendular state”:

\[
\begin{align*}
J=0 & \quad 0.87 \\
J=2 & \quad + 0.48 \\
J=4 & \quad + 0.06 \\
\tilde{J}=0 & \quad = \\
\end{align*}
\]

Field imparts a noninteger value of \( \langle J^2 \rangle \), in the example above \( \langle J^2 \rangle = 1.47 \)
Is angular momentum always quantized?

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The molecule is shaken by the field
Can one make use of it?

Weakly bound molecules usually support no rotation (no states with $J \geq 1$)

For instance, the last vibrational state of $^{85}\text{Rb}_2$ dissociates for $\langle J^2 \rangle \geq 0.27$
**Can one make use of it?**

Weakly bound molecules usually support no rotation (no states with \( J \geq 1 \))

For instance, the last vibrational state of \( ^{85}\text{Rb}_2 \) dissociates for \( \langle J^2 \rangle \geq 0.27 \).

The laser field adds a centrifugal term to the potential \( V(r) \), so that the effective potential is:

\[
U_{\text{eff}}(r) = V(r) + \frac{\langle J^2 \rangle \hbar^2}{2mr^2}
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We may tune it by changing the intensity
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What happens when we apply the laser field? Let's see...
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The laser is on...
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a bit more intensity...
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more...
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We may tune it by changing the intensity more!
Can one make use of it?

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Mikhail Lemeshko (FHI)  Probing weakly bound molecules  DPG 2010
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What about experiments?

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What about experiments?

Could the experimentalists have already seen the effect?

Yes, they could have: example 1

The intensity of some optical dipole traps reaches $10^6 – 10^7$ W/cm$^2$
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Yes, they could have: example 1

The intensity of some optical dipole traps reaches $10^6 - 10^7$ W/cm$^2$

This may have already dissociated some of the weakest-bound molecules
What about experiments?

Could the experimentalists have already seen the effect?

Yes, they could have: example 2

Lasers in optical dipole trap change the effective potential...
Could the experimentalists have already seen the effect?

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...and therefore – the binding energy
Could the experimentalists have already seen the effect?

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This may cause errors in measuring $E_b$
Could the experimentalists have already seen the effect?

Yes, they could have: example 2

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This may cause errors in measuring $E_b$
Other possibilities

- Using nonresonant fields one can change the scattering length

- Thereby, one can tune the positions of Feshbach resonances
Enhancing photoassociation of ultracold atoms

Collaboration with Ruzin Aganoglu and Christiane Koch, Freie Universität Berlin
Ruzin’s talk: Thursday 11:00, E 001
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What happens if a laser pulse is short?

“Short” means “shorter than the rotational period”
What happens if a laser pulse is short?

“Short” means “shorter than the rotational period”

For a cw-laser field, $\langle J^2 \rangle$ is constant
What happens if a laser pulse is short?

“Short” means “shorter than the rotational period”

If the pulse duration is longer than the rotational period, $\langle J^2 \rangle$ is transferred adiabatically.

![Graph showing the relationship between time (rotational periods) and intensity or $\Delta \omega$. The graph illustrates the behavior of $\langle J^2 \rangle$ over time, with peaks and troughs indicating changes in intensity or frequency difference.](image)
What happens if a laser pulse is short?

“Short” means “shorter than the rotational period”

If the pulse duration is longer than the rotational period, $\langle J^2 \rangle$ is transferred adiabatically.

The molecule has no angular momentum after the pulse has passed.
What happens if a laser pulse is short?

“Short” means “shorter than the rotational period”

If the pulse duration is shorter than the rotational period, the process is nonadiabatic.

A part of the angular momentum is transferred to the molecule forever.
What happens if a laser pulse is short?

“Short” means “shorter than the rotational period”

In the case of very short pulses most of the angular momentum is imparted forever.

This angular momentum remains unless the system is perturbed.

If the transferred angular momentum exceeds some critical value, the molecule will be shaken enough by the pulse to dissociate.
And... if the pulse is even shorter?

If the pulse duration is shorter than the *vibrational* period, the transferred angular momentum depends on the internuclear distance.
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If the pulse duration is shorter than the *vibrational* period, the transferred angular momentum depends on the internuclear distance.

Consequently, the pulse intensity needed for dissociation depends on the distance which molecule had at the moment when the laser pulse struck.

We can probe the vibrational dynamics!
And... if the pulse is even shorter?

If the pulse duration is shorter than the vibrational period, the transferred angular momentum depends on the internuclear distance.

For any intensity $I$ there is some critical distance $r^*$. 

![Graph showing the relationship between intensity and internuclear distance.]
And... if the pulse is even shorter?

If the pulse duration is shorter than the *vibrational* period, the transferred angular momentum depends on the internuclear distance.

For any intensity $I$ there is some critical distance $r^*$. If the internuclear distance is smaller than $r^*$ at the moment when the pulse strikes, the molecule dissociates.
And... if the pulse is even shorter?

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For any intensity $I$ there is some critical distance $r^*$. If the internuclear distance is smaller than $r^*$ at the moment when the pulse strikes, the molecule dissociates. No dissociation occurs for larger internuclear separations.
And... if the pulse is even shorter?

If the pulse duration is shorter than the vibrational period, the transferred angular momentum depends on the internuclear distance.

For any intensity $I$ there is some critical distance $r^*$. If the internuclear distance is smaller than $r^*$ at the moment when the pulse strikes, the molecule dissociates.

No dissociation occurs for larger internuclear separations.

So, for any pulse intensity $I$ the probability of dissociation is the probability to have internuclear distances smaller than $r^*(I)$.
And... if the pulse is even shorter?

If the pulse duration is shorter than the *vibrational* period, the transferred angular momentum depends on the internuclear distance:

This is simply the integral of the squared wavefunction:

\[
F(r^*) = \int_0^{r^*} |\phi_v(r)|^2 \, dr.
\]

![Graph showing the relationship between laser intensity and internuclear distance for dissociation and no dissociation.](graph.png)
And... if the pulse is even shorter?

If the pulse duration is shorter than the *vibrational* period, the transferred angular momentum depends on the internuclear distance.

This is simply the integral of the squared wavefunction:

$$F(r^*) = \int_0^{r^*} |\phi_v(r)|^2 \, dr.$$ 

Here comes the idea:

In an experiment we can measure $F(I)$
And... if the pulse is even shorter?

If the pulse duration is shorter than the \textit{vibrational} period, the transferred angular momentum depends on the internuclear distance.

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In an experiment we can measure \( F(I) \)

We can calculate the dependence \( I(r^*) \)
And... if the pulse is even shorter?

If the pulse duration is shorter than the vibrational period, the transferred angular momentum depends on the internuclear distance.

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Here comes the idea:

In an experiment we can measure $F(I)$

We can calculate the dependence $I(r^*)$

Hence, we can obtain the square of the vibrational wavefunction!
Outline

1. Structure of weakly bound molecules
2. Molecules in nonresonant laser fields
3. What about experiments?
4. Probing weakly bound species by short laser pulses
5. Results for weakly bound $^{85}$Rb$_2$ molecules
6. Conclusions and outlook
Results for weakly bound $^{85}\text{Rb}_2$ molecules

Potential and wavefunction

We used a single Rb$_2$ potential curve from ref. [Seto et al JCP, 113, 3067 (2000)], combining it with dispersion terms from ref. [van Kempen et al PRL 88, 093201 (2002)]

The last vibrational state, $v = 123$, is bound by $E_b = -237$ kHz

![Graph showing potential energy and wavefunction](image-url)
Dependence of dissociation probability from the intensity

The vibrational period of $^{85}\text{Rb}_2$ ($v = 123$) molecule is about 0.67 $\mu$s, so it can be probed by ns pulses. We performed the calculation for 50 ps Gaussian pulses.
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The maxima of $F(I)$ reflect the nodes of the vibrational wavefunction.
The vibrational period of $^{85}\text{Rb}_2$ ($v = 123$) molecule is about 0.67 $\mu$s, so it can be probed by ns pulses. We performed the calculation for 50 ps Gaussian pulses.

The “edge” of $F(I)$ gives the position of the wavefunction’s main maximum.
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Conclusions

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2. Using a cw-laser field one can control the atomic scattering length, positions of Feshbach resonances, and enhance the photoassociation yield.

3. Using short laser pulses, it is possible to map out the square of the vibrational wavefunction, and thus determine accurately the potential.
Conclusions

We showed that weakly bound molecules can be probed by “shaking” in nonresonant laser fields.

Using a cw-laser field one can control the atomic scattering length, positions of Feshbach resonances, and enhance the photoassociation yield.

Using short laser pulses, it is possible to map out the square of the vibrational wavefunction, and thus determine accurately the potential.

As an aside, we derived simple expressions for a number of rotational states, supported by a weakly bound molecule, and for the rotational constants.
Outlook

1. The experimentalists may have already observed some shaking due to the field of optical dipole traps.
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2. Manipulating Feshbach resonances with a cw-laser might be a straightforward proof of the shaking mechanism.
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2. Manipulating Feshbach resonances with a cw-laser might be a straightforward proof of the shaking mechanism

3. We look forward to the experiments with short laser pulses
Thank you for your attention!

Further reading:
– Phys. Rev. Lett. 103, 053003 (2009) (about probing weakly bound molecules)
– Phys. Rev. A 79, 050501 (2009) (rotational states of weakly bound dimers)
– J. At. Mol. Sci. 1, 39 (2010) (rotational states of weakly bound molecular ions)