Lecture 6   24.6.24

To figure out how to describe and
compute the properties of Rydberg molecules,
we need to figure out how to solve
<u>nonseperable</u> <u>quantum</u> <u>mechanical</u> <u>systems</u>.

One of the most efficient and conceptually
useful ways to break apart and solve a
complicated multi-dimensional problem is to
use basis expansions to convert the
problem to the solution of many coupled
1D Schrödinger equations.

The general process is as follows:
  1) Identify a fragmentation coordinate "r"
     → This is ideal for collisions, but
       also a good way to think about
       bound state calculations → even it
       it is overkill sometimes.
  2) Solve the Schrö eq for all other
     coordinates "ω" to obtain a complete +
     orthonormal basis for those "internal"
     coordinates.

$$H_\omega \, \phi_i(\omega) = \varepsilon_i \, \phi_i(\omega)$$

3) Expand the total wavefunction into this basis:

$$\Psi_\beta(r,\omega) = \frac{1}{r} \sum_i \phi_i(\omega) \, f_{\varepsilon_i}(r)$$

4) Act on this wf with the Hamiltonian H, then project onto $\langle \phi_j |$ to obtain a set of coupled equations:

$$0 = \langle\langle \phi_j | H | \Psi_\beta(r,\omega) \rangle\rangle$$

$$= -\frac{1}{2m} f''_{\varepsilon_i}(r) \, \delta_{ij} + \left(\frac{l_i(l_i+1)}{2\mu r^2} + V(r) + \varepsilon_i - E \right) f_{\varepsilon_i}(r) \, \delta_{ij}$$

note: the eigenvalues of the ω-eval equation determine the threshold energies!

$$+ \underbrace{W_{ij}}_{} f_{\varepsilon_j}$$

$$W_{ij} = \langle\langle \phi_i(\omega) | V(r,\omega) | \phi_j(\omega) \rangle\rangle.$$

If we define:
$$\vec{f} = \left(f_0(r), \, f_1(r), \, \ldots, \, f_{l_{max}}(r) \right)^\top$$
$$\vec{l}^2 = l_i(l_i+1)\, \delta_{i \varepsilon'}$$
$$\underline{1} = \delta_{\varepsilon \varepsilon'}$$

Then we have a very compact equation,

$$-\frac{1}{2m}\vec{f}''(r) + \left(\frac{\vec{\ell}^{\,2}}{2r^2} + U(r) + (\epsilon_i - E)\right)\vec{f}(r) + \underline{W}\vec{f} = 0.$$

↑ diagonal ↑
matrices

↑
coupling through
off-diagonal
terms here.

(eq. 1)

This is all just "math tricks" unless we choose the right basis. Some examples might help:

1) $e^- - H$ scattering. Here we work in the rest frame of an 'infinitely' heavy proton orbited by two electrons:

In this approximation, the total wave function can be written $\Psi(\vec{r}_1, \vec{r}_2)$ and it is determined by the Hamiltonian

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

We pick r_2 to be the fragmentation coordinate. That means that

$$H_\omega = -\frac{1}{2}\nabla_1^2 - \frac{1}{r_1} + \frac{\ell_{2i}(\ell_{2i}+1)}{2r_2^2}$$

$$W = \frac{1}{|r_1 - r_2|}$$

$$U = -\frac{1}{r_2}$$

(note: here we're ignoring spin and antisymmetrization!)

Thus, it's clear that
$$i = \{ l_{1i}, l_{2i}, n_{1i}, L_i, M_i \},$$
$$\rightarrow |\Phi_i\rangle = \frac{u_{n_{1i}}(r_i)}{r_i} \underbrace{| (l_{1i} l_{2i}) L_i M_i\rangle}_{\text{total summed}}$$

$\underbrace{}$
hydrogen
wfs

total summed
ang-mo

And so eq. 1 becomes...

$$0 = -\frac{1}{2} \vec{f}''(r_2) + \left(\frac{\vec{l_2}^2}{2r_2^2} - \frac{1}{r_2} - \frac{1}{2n^2} - E \right) \vec{f}(r_2) + \underline{W(r_1, r_2)} \vec{f}(r_2)$$

$$\text{(eq. 2)} \qquad\qquad \underset{\varepsilon_i}{\uparrow} \qquad \zeta = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} P_n(\cos\theta_{12})$$
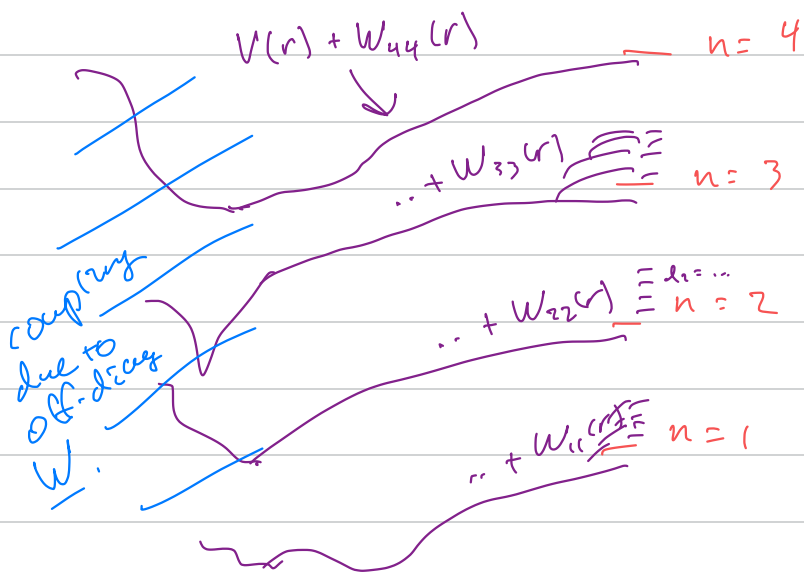
where $\underline{W(r_1, r_2)} = \langle n_{1i} l_{1i} l_{2i} L_i M_i | \frac{1}{|\vec{r_1} - \vec{r_2}|} | n_{1j} l_{1j} l_{2j} L_j M_j\rangle$

We'll come back to this when we discuss
the dispersion/polarization interaction between
an electron and an atom. But for now, just
notice what we've done: replaced a complicated
6D problem where we have <u>no</u> insight into
the structure of the component particles
into an (infinite) set of coupled 1D equations
with lots of useful structure!

What eq. 2 "looks" like is:

$$V(r) + W_{44}(r) \qquad \underline{\qquad} \quad n = 4 \qquad \text{(thresholds of the H atom)}$$

$$\cdots + W_{33}(r) \underline{\underline{\equiv}} \quad n = 3 \qquad \rightarrow \text{EACH eq. looks}$$

like an electron coming in in

$$\cdots + W_{22}(r) \underline{\overline{\equiv}}_{n = 2}^{l_1 = \cdots} \qquad$$ one channel, with

its own threshold

$$\cdots + W_{11}(r)\overline{\underline{\equiv}} \quad n = 1 \qquad$$ and potential,

then coupling to

and scattering into

other channels.

Coupling due to off-diag. $\underline{W}$.

$\rightarrow$ This describes inelastic processes!

2) H in a magnetic field:

$$H = -\frac{1}{2} \nabla^2 - \frac{1}{r} + \frac{B^2 r^2 \sin^2\theta}{8} + B \hat{L}_z$$

$\rightarrow$ This is a 2D problem in (r, θ) that was studied extensively in the 80s-90s and was instrumental in opening up the field of QUANTUM CHAOS.

3) e^- scattering off of a polar molecule

$$U(r,\theta) = \sum_{L=0}^{\infty} V_L(R) \, P_L(\cos\theta)$$

4) Rydberg molecules. Here we have

a Rydberg atom A interacting with a distant ground state atom B. The full wave function depends on the $e^- - A^+$ relative coordinate $\vec{r}$ and the A-B relative coordinate $\vec{R}$. Throwing away mass-polarization terms as usual, we are left with

$$H = -\frac{1}{2\mu}\nabla_R^2 - \frac{1}{2m}\nabla_r^2 + V_r(\wedge) + V_R(R) + U(r,R)$$

⌣: kinetic energy + nuclear interaction (weak!)

⌣: kinetic energy + atom interaction (coulomb)

⌣: e⁻ - groundstate atom interaction,

　　i.e. the Fermi Pseudopotential!

Here we might have some options for
our fragmentation coordinate, depending
on the type of process we want to study.
We could pick $\underline{r}$, and then we describe
Rydberg states of the AB molecule /
photoionization.

But now we want the Rydberg electron to
stay attached to A⁺, and describe molecular
formation- is motion bounded as $R \to \infty$?
therefore we pick R as the frag-coord.

$$\rightarrow H_\omega = \smile + \frac{l(l+1)}{2n^2}$$

$$W = \smile$$

$$V = V_R(R)$$

And, $c = \{\underbrace{n, l, m}_{\text{Rydberg atom}}, \overbrace{L, M}^{\text{Nuclear rotation}}\}$

D.F

$$\Rightarrow \Phi_c(\omega) = |n l m\rangle |L M\rangle.$$

So, eq. 1 is: e.g. $V_R(R)$

$$0 = -\frac{1}{2\mu}\vec{f}''(R) + \left(\frac{\vec{L}^2}{2\mu R^2} - \frac{\alpha}{2R^4} - \frac{1}{2(n-n_e)^2} - E\right)\vec{f}(R)$$
$$+ \underbrace{\langle n l m | 2\pi a_s \delta^3(\vec{r} - \vec{R})|n'l'm'\rangle}_{W} \vec{f}(R).$$

(eq. 3)

To simplify the following, let's take $L = M = 0$ (note that $\hat{R}$ separates), assume $\alpha/2R^4$ is negligible, ignore q-defects, and measure E relative to $-\frac{1}{2n^2}$. Then eq. 3 becomes:

$$0 = -\frac{1}{2\mu}\vec{f}''(R) + (W - E\mathbb{1})\vec{f}(R).$$

This is usually not the eq. we want to work with here - especially for Rydberg molecules where the dimension grows with n!

So let's prepare an adiabatic approximation to these close-coupling / coupled-channel equations.

For each R value, we can diagonalize $\underline{W}$:

$$\underline{W} = \underline{S}\,\underline{U}\,\underline{S}^{-1} \quad , \text{ where } \quad \underline{U} \equiv \underline{U}(R) \text{ , etc.}$$

Inserting this and several $\underline{1} = \underline{S}\,\underline{S}^{-1}$, we get

$$0 = -\frac{1}{2\mu}\frac{d^2}{dR^2}\left(SS^{-1}\right|\vec{f}(R)) + \left(SUS^{-1} - E\,SS^{-1}\right)\vec{f}(R)$$

$$= -\frac{1}{2\mu}\frac{d^2}{dR^2}\left(S\,\tilde{\vec{f}}(R)\right) + S\left(U - E\right)\tilde{\vec{f}}(R),$$

$$\tilde{\vec{f}} = S^{-1}\vec{f}.$$

$$\rightarrow 0 = S^{-1}0 = -\frac{1}{2\mu}S^{-1}\frac{d^2}{dR^2}\underbrace{\left(S\tilde{\vec{f}}(R)\right)} + \left(U(R) - E\right)\tilde{\vec{f}}(R)$$

$$= \left(S'\tilde{\vec{f}} + \tilde{\vec{f}}\,S\right)' = S''\tilde{\vec{f}} + 2S'\tilde{\vec{f}}' + S\tilde{\vec{f}}''$$

So finally, after this change of basis at every R value, we have a new set of coupled eqns:

$$0 = -\frac{1}{2\mu}\tilde{\vec{f}}''(R) + \underbrace{\left(U(R) - E\right)}_{\text{diagonal!}}\tilde{\vec{f}}(R) - \frac{1}{2\mu}\underbrace{\left(2\underline{P}\frac{d}{dR} + \underline{Q}\right)}_{\text{derivative coupling!}}\tilde{\vec{f}}(R)$$

Let's switch to a slightly more familiar notation now, where $\phi_\mu(R)$ is the eigenvector (of channel functions) corresponding to the potential curve $U_\mu(R)$. Then we have:

$$0 = \sum_\nu \left(-\frac{1}{2\mu} \frac{d^2}{dR^2} \delta_{\mu\nu} + U_{\nu\nu}(R) - E\delta_{\mu\nu} \right) \tilde{f}_\nu(R)$$

$$+ \sum_\nu \left(2 P_{\mu\nu} \frac{d}{dR} + Q_{\mu\nu} \right) \tilde{f}(R)$$

$$P_{\mu\nu} = \langle \phi_\mu | \frac{d}{dR} | \phi_\nu \rangle$$

$$Q_{\mu\nu} = \langle \phi_\mu | \frac{d^2}{dR^2} | \phi_\nu \rangle$$

The top row describes uncoupled vibrational motion on individual potential curves - if we drop the bottom row entirely, this is nothing more than the Born-Oppenheimer approximation!

$V(R)$

$U_3(R)$

R

$U_2(R)$

$U_1(R)$

$\tilde{f}_{12}(R)$

$\tilde{f}_{11}(R)$
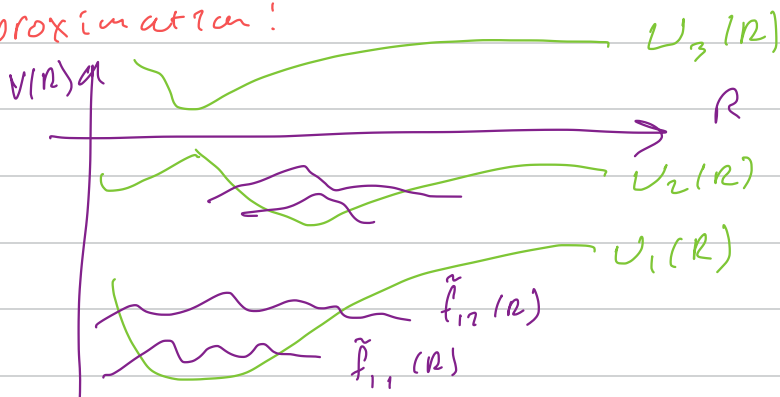
How good of an approximation is it to totally drop the second row?

$\Rightarrow$ Often VERY good!

To understand why, let's derive 2 identities:

1) $\dfrac{dP}{dR} = \dfrac{d}{dR} \langle \phi_{\mu} | d_R \phi_{\nu} \rangle$

$= \underbrace{\langle d_R \phi_{\mu} | d_R \phi_{\nu} \rangle}\ + \underbrace{\langle \phi_{\mu} | d_R^2 \phi_{\nu} \rangle}_{Q_{\mu\nu}}$

This first term is:

$= \sum_q \langle d_R \phi_{\mu} | d_q \rangle \times \langle \phi_q | d_R \phi_{\nu} \rangle$

$\underbrace{}_{\text{identity}}$

$= P_{\mu q}\, P_{q\nu} = P^2$

So: $dP/dR = \underline{P^2} + \underline{Q}$.

2) Since $H_\omega\, \phi_\nu(R) = U_\nu(R)\, \phi_\nu(R)$

$\Rightarrow \nabla(H\phi) = \left(\dfrac{dH}{dR}\right)\phi_\nu + H\phi' = U_\nu'\, \phi_\nu + U_\nu\, \phi_\nu'$

Next we project onto $\langle \phi_\mu |$:

$$\rightarrow \langle \phi_\mu | H' | \phi_\nu \rangle + \langle \phi_\mu | H | \phi_\nu' \rangle = U_\nu' \underbrace{\langle \phi_\mu | \phi_\nu \rangle}_{S_{\mu\nu}} + U_\nu \underbrace{\langle \phi_\mu | \phi_\nu' \rangle}_{P_{\mu\nu}}$$

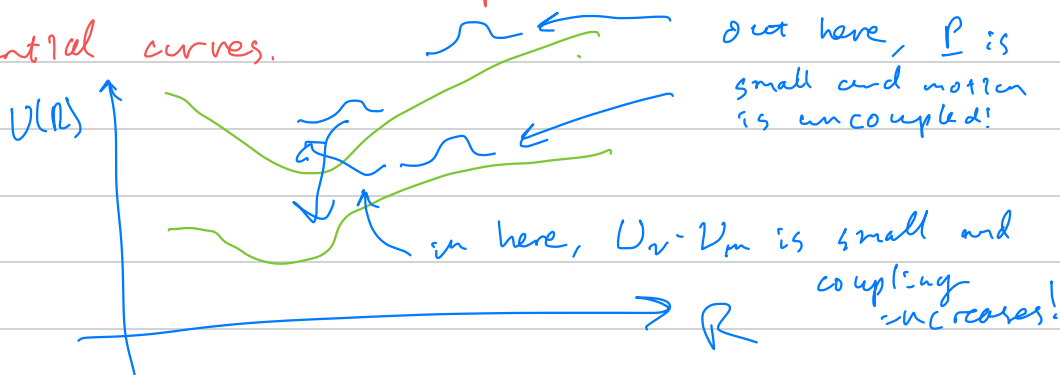$$\underbrace{\langle \phi_\mu | H | \phi_\nu' \rangle}_{U_\mu \langle \phi_\mu |}$$

$$\langle \phi_\mu | H' | \phi_\nu \rangle = - U_\mu P_{\mu\nu} + U_\nu' \overset{0}{S_{\mu\nu}} + U_\nu P_{\mu\nu}$$

$$\rightarrow \quad P_{\mu\nu} = \frac{\langle \phi_\mu | H' | \phi_\nu \rangle}{U_\nu (R) - U_\mu (R)}$$

These two results tell us: the strength of
Q depends on the strength of $P \Rightarrow$ and
also on how quickly it varies w/ R.

Furthermore, the strength of $\underline{P}$ depends on
how quickly the Hamiltonian changes with R and,
most crucially, on the separation between adiabatic
potential curves.

$U(R)$

out here, $\underline{P}$ is
small and motion
is uncoupled!

in here, U_ν-U_m is small and
coupling
increases!

R

So: back to Ryd-Mol(s)!

This is basically the scenario of the
Fermi pseudopotential derivation - just
with fewer atoms involved and, crucially,
ultracold temperatures. Why? We'll see soon.

- From Fermi PP derivation: whatever
  the "real" electron-atom potential is,
  we can replace it with the Fermi PP (+
  higher L pieces):

$$U(\vec{r},\vec{R}) = 2\pi a_s \delta^3(\vec{r}-\vec{R}) + 6\pi a_p^3 \overleftarrow{\nabla} \delta^3(\vec{r}-\vec{R})\vec{\nabla} + \ldots$$

Next, remember our coupled channel formalism.
We know the states of the Rydberg atom, so
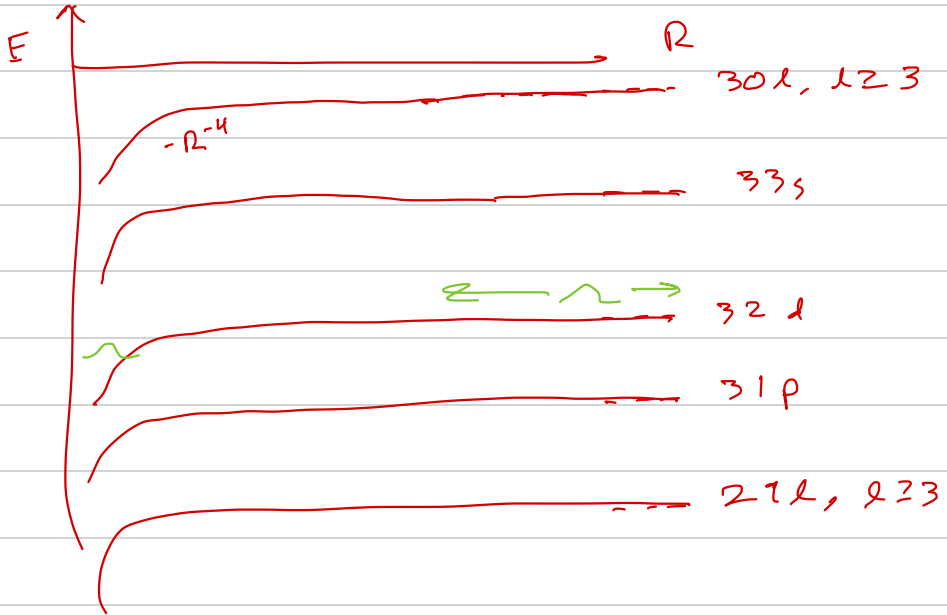they make an obvious choice for the channels.

$$\Psi(\vec{r},\vec{R}) = \sum_i \frac{f_i(R)}{R} |n l m, N M_N\rangle$$

From our derivation in Lec. 9..... this
leads to the coupled eqns...

$$0 = -\frac{1}{2\mu} f_i''(R) + \left[\frac{N^2}{2\mu R^2} - \frac{\alpha}{2R^4} - \left(E + \frac{1}{2(n-\mu_c)^2} \right) \right] f_i(R)$$
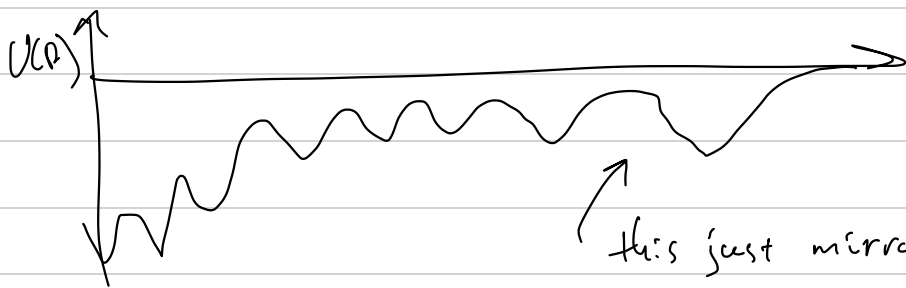
$$V_{ii'} \, f_{i'}(R)$$

Pectorially,

Without the electron-atom interaction, motion occurs along uncoupled potentials w/ only very short-range potentials.

Let's check out the electronic-state dependant potential matrix.

$$\underline{V} = -\frac{1}{2(n-\mu_\ell)^2} + 2\pi a_s \, \Psi^*_{n\ell m}(R)\Psi_{n\ell'm'}(R) + 6\pi a_p \, \Psi'^*_{n\ell m}(R)\Psi'_{n\ell'm'}(R)$$
$$+ \dots$$

when $\mu_\ell \neq 0$: we have good reason to
consider these low-ℓ states endividually.

$$\rightarrow V_{\ell \leq 2} = -\frac{1}{2(n-\mu_\ell)^2} + 2\pi a_s |\Psi|^2 + 6\pi a_p |\Psi'|^2 + \dots$$

this just mirrors the
Rydberg wavefunction (s-wave
limit)

$\rightarrow$ Note that this is a slightly different
perspective than usual Born-Oppenheimer.
It's actually a diabatic calculation!

Since $1 = \int \Psi^2 \, dV \approx \Psi^2 \cdot \frac{4}{3}\pi (2n^2)^3$,
$$\Psi^2 \sim n^{-6}.$$
$\Rightarrow$ These potentials are weak!

For high l, we can no longer argue that these couplings are negligible as there are no energy separators to help out any more...

$\rightarrow$ we have a coupling matrix

$$V_{ll'} = \langle nlm | 2\pi a_s \delta^3 + 6\pi a_p^3 \nabla \delta^3 \nabla | n l'm \rangle$$

to treat.

It now makes sense to move to a representation where this is diagonal. $\rightarrow$ BO approx!

We can actually use SUSY to diagonalize this (well, kind of). Note the following:

$$V_{ll'} = 2\pi a_s \, \phi_{nl}^*(R) \, \phi_{nl'}(R) + 6\pi a_p^3 \phi_{nl}^{'*}(R) \, \phi_{nl'}'(R) + \dots$$

Let: $A_{l0} = \sqrt{2\pi a_s} \, \phi_{nl}^* \rightarrow A_{0l'}^\dagger = \sqrt{2\pi a_s} \, \phi_{nl'}(R)$

$A_{l1} = \sqrt{6\pi a_p} \, \phi_{nl}^{'*} \rightarrow A_{1l'}^\dagger = \sqrt{6\pi a_p} \, \phi_{nl'}'(R)$

So: $V_{ll'} = \sum_{L=0}^{1} \tilde{A}_{lL} A_{Ll'}^\dagger$!

That should ring some bells. Remember
that we showed that

$$H^{(1)} = A A^\dagger \quad \text{and} \quad H^2 = A^\dagger A$$

have __degenerate__ spectra!

So: we can just diagonalize $H^{(2)} = A^\dagger A$
to get the (non-zero) eigenvalues!!!
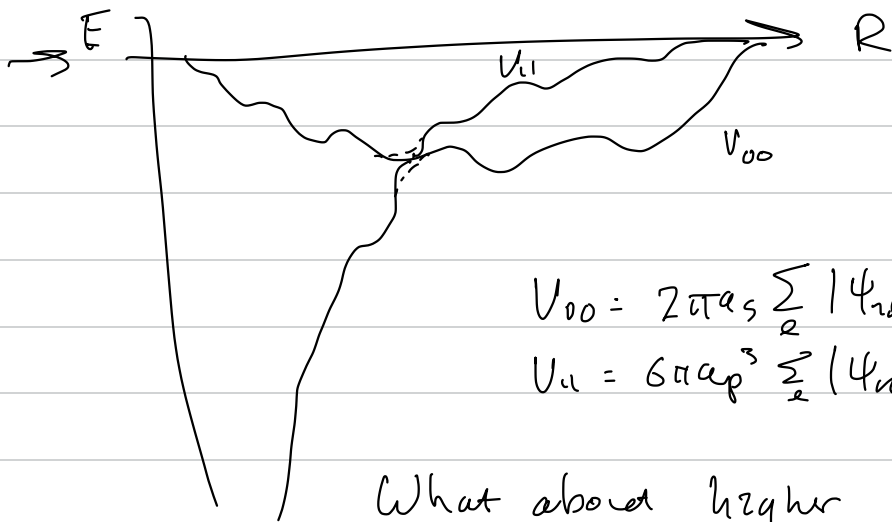
$$V_{00} = 2\pi a_s \sum_e |\psi_{n\ell o}(R)|^2$$
$$V_{11} = 6\pi a_p^3 \sum_e |\psi'_{n\ell o}(R)|^2.$$

What about higher L?

In a nutshell: since
$$\delta_L \sim k^2$$
we know how __all__ of these will behave!