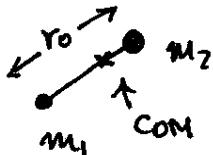


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First example of a central force problem: A rigid rotor. Classically

a R.R. is 2 masses constrained to have a const. dist. between them:



$$\frac{1}{M} = \frac{1}{m_1} + \frac{1}{m_2} \quad M = \text{reduced mass}$$

$$I = Mr_0^2 = \text{moment of inertia.}$$

It's an example of a central force problem because the constraint $r=r_0$ can be thought of as due to a sharply confining potential centered at $r=r_0$. The classical energy is

$$E = \frac{L^2}{2I},$$

suggesting that the qu. energy should be

$$E_\ell = \frac{\ell(\ell+1)\hbar^2}{2I}.$$

It depends on ℓ . A guess is that the wavefn. for the relative motion ($\vec{r} = \vec{r}_2 - \vec{r}_1$) is

$$\psi_{\ell m}(\vec{r}) = \delta(r-r_0) Y_m(\theta, \phi).$$

Rigid bodies are an idealization that doesn't exist in nature, but diatomic molecules exist and have many similar features. Consider for example CO. The masses are $m_C \approx 12m_H$, $m_O \approx 16m_H$, $m_H =$ mass of hydrogen $\approx 2000 m$, $m =$ electron mass. Then

$$M = \text{reduced mass} \approx 7m_H \approx 10,000 m$$

very roughly. This makes some small parameters:

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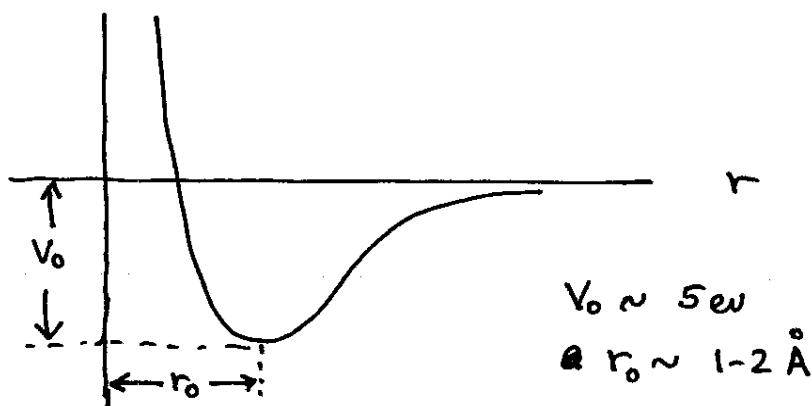
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$$\left. \begin{array}{l} \frac{m}{M} \sim \frac{1}{10000} \\ \sqrt{\frac{m}{M}} \sim \frac{1}{100} \\ \left(\frac{m}{M}\right)^{1/4} \sim \frac{1}{10} \end{array} \right\}$$

Roughly these values apply for most diatomic molecules.

The diatomic molecule is a central force problem because the atoms interact by means of a potential $V(r)$. It has the general shape:

$$V(r)$$



As shown, the well depth is V_0 and radius of min is r_0 , with typical values shown. At large distances the interaction is electrostatic: each atom induces a dipole moment in the other, and they attract. At shorter distances, where electron clouds start to overlap, there arises a repulsive force due to exchange, that is, when you force electron clouds to occupy the same region of space, by the Pauli principle the momenta go up and energy is required. This explains the hard repulsive wall

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at small r . There is no simple analytical form for $V(r)$, so we will rely on crude order-of-magnitude estimates that follow from dimensional analysis.

The basic fact we rely on is that the potential is determined by the dynamics of the electron clouds alone. There are only 3 physical constants that enter into the electron dynamics: e, m, \hbar . c is not in the list because the interaction is electrostatic and the motion nonrelativistic.

Using e, m, \hbar it is possible to construct a unique length, energy, time, etc. These are:

$$\text{length } a_0 = \frac{\hbar^2}{me^2} = 0.5 \text{ \AA}$$

$$\text{energy } K_0 = \frac{me^4}{\hbar^2} = 27 \text{ ev.} = \frac{e^2}{a_0}$$

$$\text{velocity } v_0 = \frac{e^2}{\hbar} = \alpha c = \frac{1}{137} c$$

$$\text{time: } T_0 = \frac{\hbar^3}{me^4} = 2 \times 10^{-17} \text{ sec.}$$

etc. Here $\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$ is the fine structure const. As an order of magnitude, these must be the distance, energy, etc. scales of the molecular potential. The estimates are crude: a_0 is about $1/3$ r_0 , and $K_0 \approx 5V_0$. We'll use them

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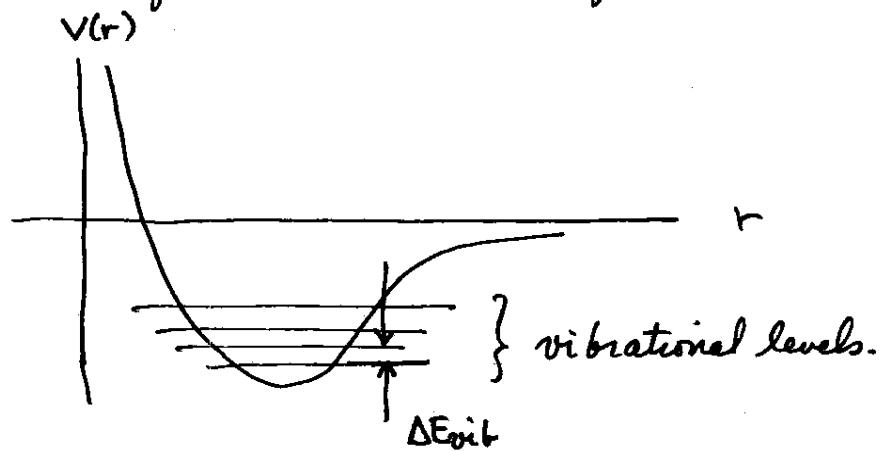
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anyway.

The radial Sch. eqn. is

$$-\frac{\hbar^2}{2M} \frac{d^2f}{dr^2} + \left[\frac{\ell(\ell+1)\hbar^2}{2Mr^2} + V(r) \right] f = Ef.$$

At first we take $\ell=0$, so we get a 1D Sch. eqn. with potential $V(r)$. Since this is a well we expect bound states, which physically are the quantized vibrations of the molecule.



The well can be approximated near the bottom by a H.O. potential, presumably only a good approx. for small vibrational quantum numbers:

$$V(r) \approx \frac{1}{2} M \omega^2 (r - r_0)^2$$

where ω = freq. of vibrations (M = reduced mass again).

We can estimate ω by supposing that when $r - r_0 \sim r_0$ (or a_0), then $\frac{1}{2} M \omega^2 (r - r_0)^2 \sim V_0$ (or K_0). Thus, ignoring the $1/2$, we write

$$M \omega^2 a_0^2 = K_0,$$

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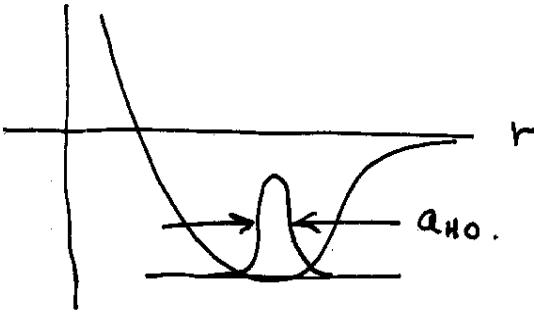
$$\text{or } \omega^2 = \frac{1}{M} \frac{K_0}{a_0^2} = \frac{1}{M} \frac{e^2}{a_0^3} = \frac{m}{M} \frac{m^2 e^8}{\hbar^6}.$$

This gives

$$\Delta E_{\text{vib}} = \hbar\omega = \sqrt{\frac{m}{M}} \frac{me^4}{\hbar^2} = \sqrt{\frac{m}{M}} K_0.$$

Thus, the vibrational level separation is down by a factor of $\approx \frac{1}{100}$ from K_0 or V_0 , and we estimate that there are perhaps 100 bound states altogether of molecular vibration.

In the vibrational ground state the wave function is a Gaussian of some width a_{HO} . (HO = harmonic osc.). We can estimate a_{HO} using some results from HO theory:



$$a_{HO} = \sqrt{\frac{\hbar}{M\omega}} = \left(\frac{m}{M}\right)^{1/4} a_0, \approx \frac{1}{10} a_0.$$

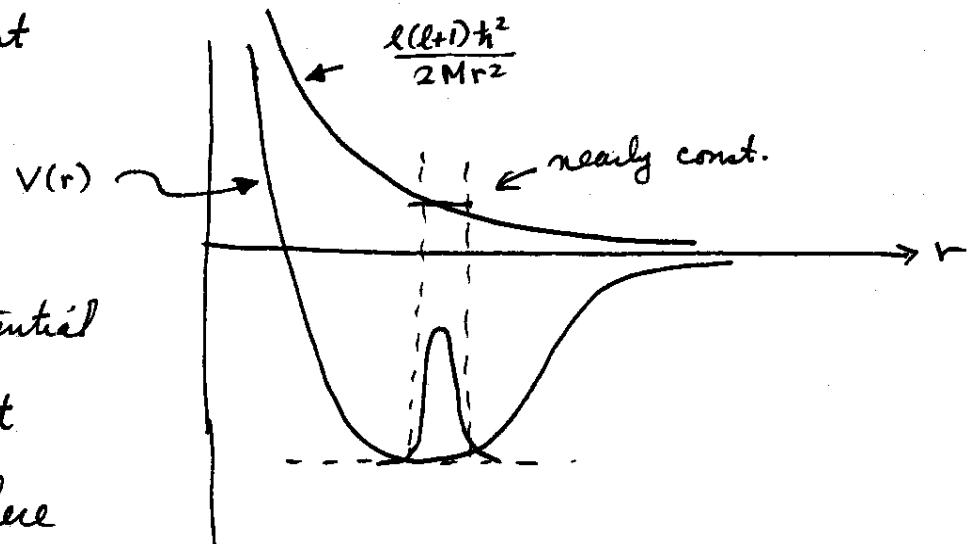
using above estimates for ω . Thus the wave fn. occupies perhaps 10% of the bond length r_0 . The molecule does behave like a rigid rotor at least approximately, because the interparticle separation lies within a narrow range near r_0 .

To take account of the case $l \neq 0$, we must include

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the centrifugal potential. But since the wave fn occupies only a small part of the r -axis near r_0 ,

the centrifugal potential is nearly constant over the region where the wave fn. is nonzero, and we can just replace r by r_0 in the centrif. pot.:



$$\frac{l(l+1)h^2}{2Mr^2} \rightarrow \frac{l(l+1)h^2}{2Mr_0^2} = \frac{l(l+1)h^2}{2I},$$

where I is the moment of inertia in the equilibrium posn. This approx. is not as good when n and l get large. Thus the Sch. eqn. becomes

$$-\frac{\hbar^2}{2M} \frac{d^2f}{dr^2} + \left[\frac{l(l+1)h^2}{2I} + \frac{1}{2}M\omega^2(r-r_0)^2 \right] f = Ef.$$

It's a H.O. Hamiltonian w. shifted origin and a const. term (the centrif. pot.) added. The energy eigenvalues are immediate:

$$E_{nl} = (n + \frac{1}{2})\hbar\omega + \frac{l(l+1)h^2}{2I}.$$

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They depend on (nl) , as expected for generic radial potentials.

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Let's examine the spacing betw. rotational energy levels.

Define ΔE_{rot} as spacing betw. $l=0$ and $l=1$ levels:

$$\Delta E_{\text{rot}} = \frac{\hbar^2}{2I} \sim \frac{\hbar^2}{M Q_0^2} = \frac{m}{M} K_0 \sim \frac{1}{10000} K_0.$$

This is $\frac{1}{100}$ times smaller than ΔE_{rib} .

so we have 3 energy scales:

K_0 : electronic, dissociation optical

$$\Delta E_{\text{vib}} \sim \sqrt{\frac{m}{M}} K_0 : \text{ vibrations} \quad \text{near-mid IR}$$

$$\Delta E_{\text{rot}} \sim \frac{m}{M} K_0 \quad \text{rotations} \quad \text{for IR- } \mu\text{-wave.}$$

Greenhouse gases absorb IR radiation from the earth by making vibrational transitions. O_2 and N_2 don't do this because being homonuclear they have no dipole moment, hence do not have electric dipole transitions.

The above is the basic set of facts about the spectra of diatomic molecules. The more sophisticated theory is called the Born-Oppenheimer approximation.

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Now we consider hydrogen and hydrogen-like (one-electron) atoms, including

$$H, He^+, Be^{++}, \dots, U^{91+}, \dots$$

We will use a spinless, electrostatic, nonrelativistic model with potential $V(r) = -Ze^2/r$, what we will call the Bohr-Schrödinger model.

We begin with atomic units. These are units such that $m = e = \hbar = 1$, commonly used in atomic physics. In A.U., the quantities a_0 etc. introduced above all become unity:

$$a_0 = \frac{\hbar^2}{me^2} = 0.5 \text{ Å} = \text{Bohr radius}$$

$$K_0 = \frac{me^4}{\hbar^2} = 27 \text{ ev} = 2 \times \text{binding energy of H.}$$

$$v_0 = \frac{e^2}{\hbar} = \alpha c = \frac{1}{137} c = \text{velocity of electron in ground state of H.}$$

$$T_0 = \frac{\hbar^3}{me^2} = 2 \times 10^{-17} \text{ sec} = \frac{2\pi}{c} \text{ period of orbital motion of electron in ground state of H.}$$

Notice in particular v_0 . The electron is fast but still mostly nonrelativistic. Notice, in A.U. $c = \frac{1}{\alpha} = 137$ (speed of light).

The radial Sch. eqn. for H-like atom is

$$-\frac{\hbar^2}{2\mu} \frac{d^2f}{dr^2} + \left[\frac{\ell(\ell+1)\hbar^2}{2\mu r^2} - \frac{Ze^2}{r} \right] f = Ef,$$

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where $\mu =$ reduced (electron-nucleus) mass. To put this eqn into dim'less form, we introduce modified atomic units, for which

$$\sqrt{Ze^2} = \cancel{\mu} = \cancel{\hbar} = 1.$$

Since $\mu \approx m$, the main change is $e^2 \rightarrow Ze^2$. In modified A.U. the units are

$$\text{length} = a = \frac{\hbar^2}{\mu Ze^2} \approx \frac{a_0}{Z}$$

$$\text{energy} = K = \frac{\mu Z^2 e^4}{\hbar^2} \approx Z^2 K_0$$

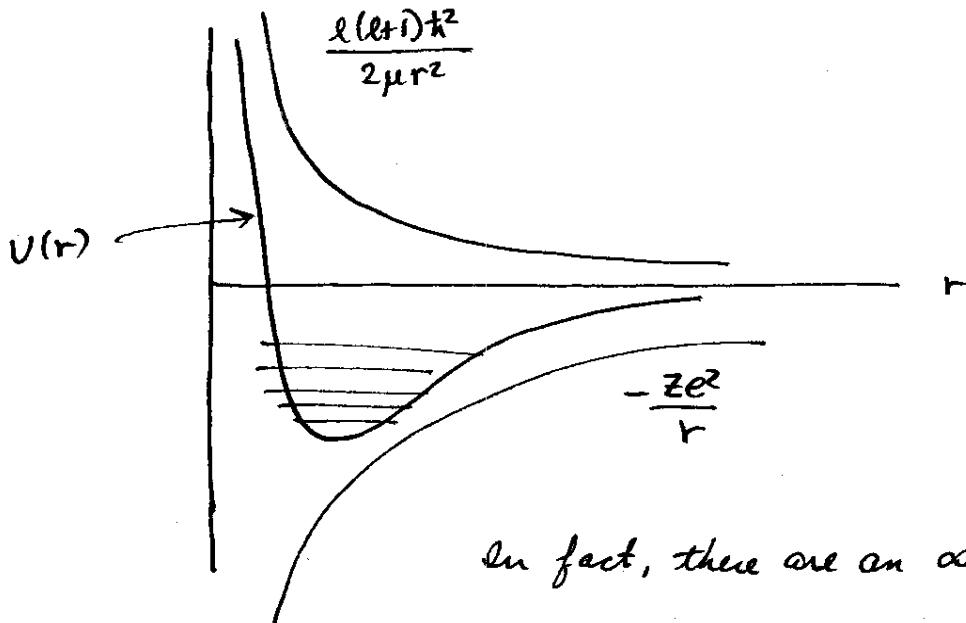
$$\text{velocity } v = \frac{Ze^2}{\hbar} = (Za)c = Zv_0.$$

etc. Notice the unit of velocity, $\frac{v}{c} = Za$. For H this is small ($1/137$) but for U it is $92/137 \approx 0.6$. For heavy atoms, the nonrelativistic Sch. eqn is not a good appx.

In modified A.U., the Sch. eqn. becomes

$$\frac{d^2f}{dr^2} + \left[-\frac{l(l+1)}{r^2} + \frac{2}{r} + 2E \right] f = 0.$$

Before analyzing, look at the potentials. The true Coulomb potential dominates at large r , the centrif at small r , creating a well for bound states:



In fact, there are an ∞ # of bound states.

There are also continuum states (for any $E \geq 0$).

Let's look for bound states, $E < 0$. We set

$$\nu = \frac{1}{\sqrt{-2E}}, \quad p = \frac{2r}{\nu}, \text{ modified radial var.}$$

Sch. eqn. becomes

$$\frac{d^2 f}{dp^2} + \left[-\frac{l(l+1)}{p^2} + \frac{\nu}{p} - \frac{1}{4} \right] f = 0. \quad (\text{RSE})$$

Standard techniques show that you only get a square-integrable solution when $\nu = n = \text{an integer in the range}$,

$$n = l+1, l+2, \dots, \infty$$

where we are thinking of l as given since it's a parameter of the RSE. n is the principal qu. #. The wave fns are

$$f_{nl}(p) = p^{l+1} e^{-p/2} L_{n+l}^{2l+1}(p)$$

↑ assoc. Laguerre polynomial.

Note that they are polynomials times exponentials $e^{-p/2}$.

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The energies are

$$E_n = -\frac{1}{2n^2},$$

indep. of l . The fact that E_n is indep. of l is due to the extra symmetry possessed by Coulomb potential. Any non-Coulomb radial potential introduced as a perturbation will restore the l -dependence.

Thinking of n as given first, then the allowed ranges on quantum numbers are

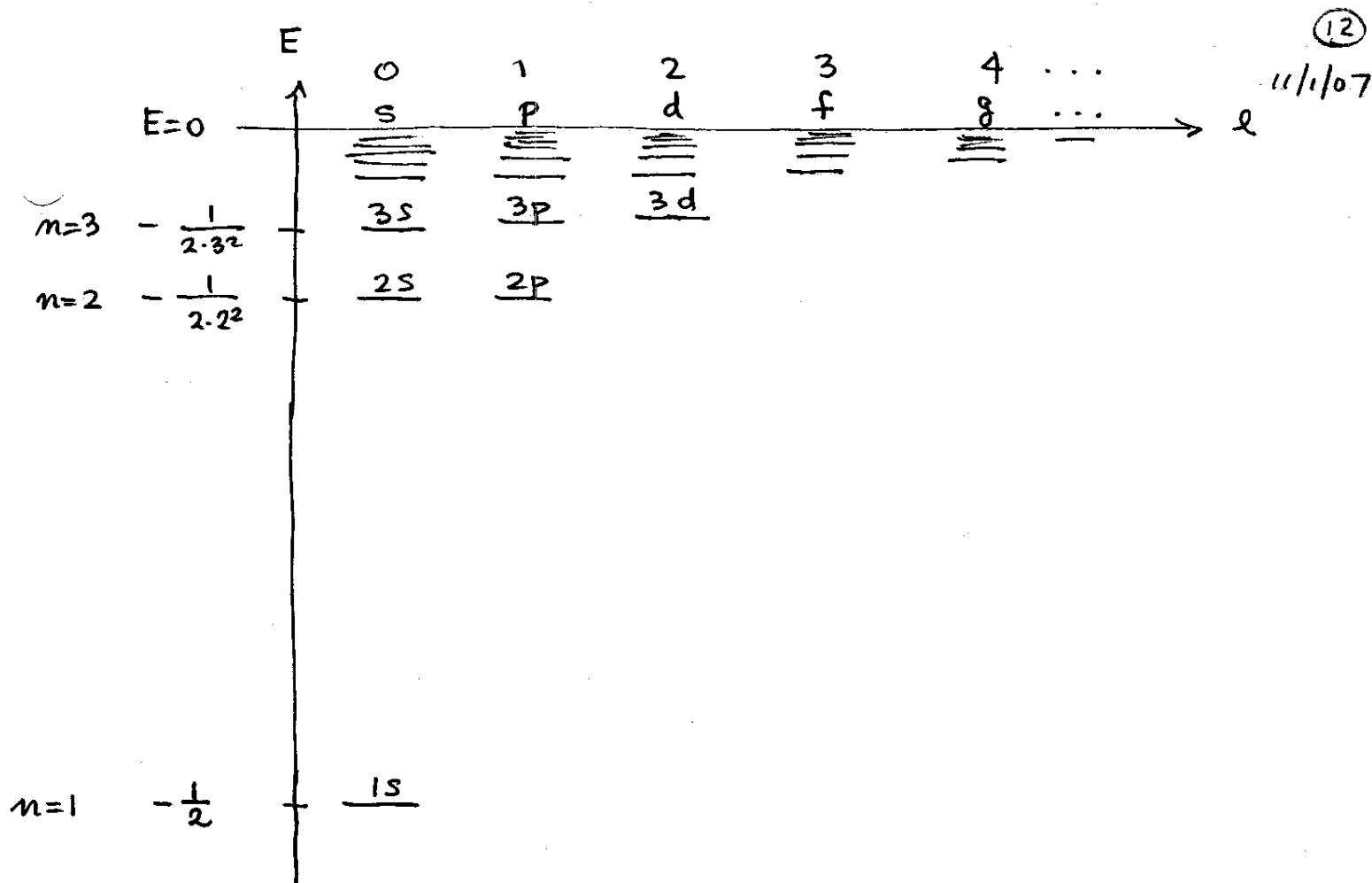
$$n = 1, 2, 3, \dots \quad \infty$$

$$l = 0, 1, \dots, n-1.$$

The degeneracy is

$$\text{degen}(E_n) = \sum_{l=0}^{n-1} (2l+1) = n^2.$$

The energy levels are traditionally arranged in a Grotius diagram, basically one for which the horizontal axis is ang. mom. and the vertical energy. $E=0$ is at the top since we're interested in bound states with $E < 0$. The angular momentum values are traditionally indicated by their letter codes s,p,d,f, etc.



An ∞ # of levels accumulate near $E=0$ in each column.

The symbols $2s, 3p$ etc. label an n and l value, hence a set of $2l+1$ states. The levels across each row are equal in energy, because of the extra degen. in H.

Interesting ways of breaking the l -degeneracy include the following. First, the volume effect modifies the $1/r$ potential by taking account of the fact that the charge in the nucleus is not a point, but spread out over the volume of the nucleus. This causes the Coulomb singularity to be smoothed out. The volume effect mainly affects the s-states, raising their

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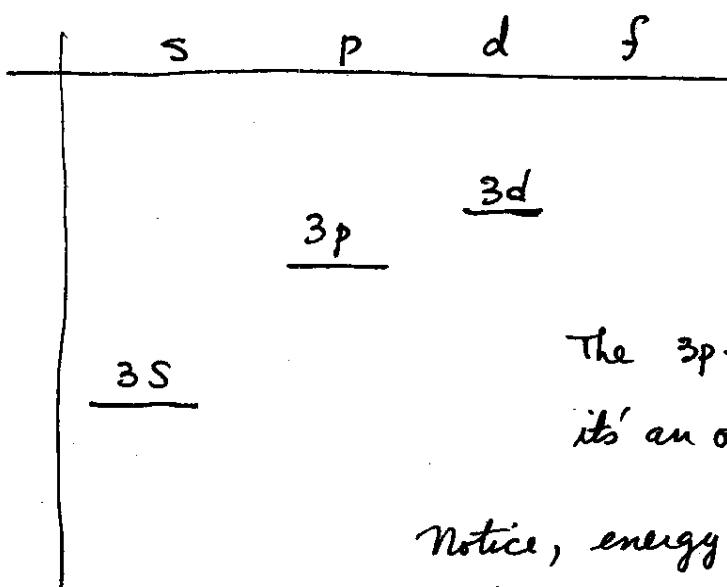
energy, since only s-waves are $\neq 0$ at $r=0$. But it
does introduce an l -dependence to the energy levels.

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Another way is to look at alkali atoms. ~~H~~: Li, Na, K, Rb, Cs, Fr.
which have a single electron outside closed shells. A model for
alkalis treats them as single electron systems, moving in a
screened potential,

$$V(r) \sim \begin{cases} -\frac{Ze^2}{r}, & r \rightarrow 0 \\ -\frac{e^2}{r}, & r \rightarrow \infty \end{cases}$$

since for small r there is no screening and for large r the
electron sees a nucleus+core w. charge -1. This potential
is not even close to a single Coulomb potential since Z_{eff} is a
rapid fn. of r inside the core. For example, in Na you
have the diagram,



There are no $n=1, 2$
levels for Na, because
the core states are
filled.

The $3p-3s$ splitting is not small,
it's an optical transition.

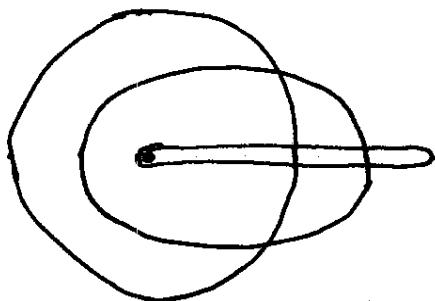
Notice, energy levels are E_n
(the generic form).

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The rule $l=0, \dots, n-1$ in H-like atoms has

a classical rationale. Consider classical motion in the force center $F = -\frac{k}{r^2}$, $k = Ze^2$ for our problem. Three classical orbits of the same energy might look like this:



These are 3 ellipses with same semi-major axis a . For the circle, $r=a$. The classical energy is a fn. only of the semi-major axis:

$$E = -\frac{k}{2a}.$$

The 3 ellipses differ however in their angular momentum. The thin orbit (eccentricity $e=1$) has $L=0$, while the circular one has $L=L_{\max}$, the maximum value L can have for the given E . In fact, it's easy to show that

$$L_{\max} = \sqrt{mk\alpha^2} = \sqrt{\frac{mk^2}{(-2E)}}.$$

This classical relation $0 \leq L \leq L_{\max}(E)$ is exactly the analog

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of $l=0, \dots, n-1$ in QM. Thus the states $l=n-1$ 11/1/07
 correspond to circular orbits, while those for $l=0$ correspond
 to the needle orbits. The needle orbits extend out twice as
 far as the circular orbits, and also extend in to the nucleus.
 You can see all of this in the plots of some radial wave
 functions, e.g. for $n=3$, $l=0, 1, 2$:

