

0.1 Multi-Electron Atoms

What we expect from perturbation theory from the non-interacting model of these energy shells is

n	ℓ	Degeneracy	N
1	0	2	2
2	0,1	$2(1+3)=8$	$2+8=10$
3	0,1,2	$2(1+3+5)=18$	$2+10+18=28$
4	0,1,2,3	$2(1+3+5+7)=32$	$2+8+18+32=60$

What is the origin of this degeneracy though? in m , it's clear that this comes from rotational invariance of the hydrogen atom, but for ℓ , it's much less clear. Turns out there's an $SO(4)$ symmetry in the hydrogen atom.¹ It's no bueno in experiment. It holds for $n = 1, 2$ for hydrogen and neon, but for argon, it sucks! We get $n = 3, N = 18$. No Bueno! Brief overview of s, p, d, f notation. We can take the next row of the PTE

Z	3	4	5	6	7	8	9	10
	Li	Be	B	C	N	O	F	Ne
He	$2s^1$	$2s^2$	$2s^2 2p^1$	$2s^2 2p^2$	$2s^2 2p^3$	$2s^2 2p^4$	$2s^2 2p^5$	$2s^2 2p^6$

But why the heck is, for instance, in Argon, and it's rows, is the $4s$ orbital filled before the $3d$ orbital? An electron in a MEA feels an effective potential of

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

The self-consistent approach to solving this problem is to iteratively solve for better and better approximations of this, using some interpolating function to get $U(r)$ to exhibit this behavior.²

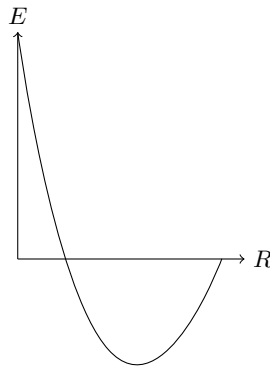
0.2 H_2



This has some hamiltonian

$$H = \frac{p^2}{2m} - \frac{e^2}{|r - \frac{R}{2}|} - \frac{e^2}{|r + \frac{R}{2}|} + \frac{e^2}{|R|}$$

What we want to find is some ground state energy of this H . We think it's probably going to look something like



The full wavefunction is going to be

$$|\psi(R)\rangle = |\psi_e\rangle \otimes |R/2\rangle \otimes |-R/2\rangle$$

We can pick some non-orthogonal set of states $|1\rangle, |2\rangle$, which are the states where we ignore the existence of proton 1, 2 antirespectively, and compute the behavior of the electron about each remaining proton. We can express this as

$$|\varphi_e^\pm\rangle = |1\rangle \pm |2\rangle$$

where

$$\begin{aligned} \langle x|1\rangle &= \varphi_{100}\left(x - \frac{R}{2}\right) \\ \langle x|2\rangle &= \varphi_{100}\left(x + \frac{R}{2}\right) \end{aligned}$$

We like this, because it's symmetric under permutation. We're going to treat R as our variational parameter. Since we haven't actually normalized our state, we need to divide through by the normalization in perturbation theory, so we get

$$E_\pm(R) = \frac{\langle \psi^\pm | H | \psi^\pm \rangle}{\langle \psi^\pm | \psi^\pm \rangle} = \frac{1}{\langle \psi^\pm | \psi^\pm \rangle} (\langle 1 | H | 1 \rangle + \langle 2 | H | 2 \rangle \pm (\langle 1 | H | 2 \rangle + \langle 2 | H | 1 \rangle))$$

¹TODO: for fun, read weinberg paper

²TODO: Look up Hartree-Fock approximation/Self-consistent field method.