

7 Atomic Structure II

To find the various states of a given atom and guess their ordering without actually doing the variational or other numerical calculations of the wavefunctions is a bit of a black art, but we can use some of the principles we developed in the *He* case. Try them on Lithium.

7.1 Lithium

Lithium is next simplest in periodic table, with $Z=3$, $A=7$. Pauli P. forbids $1s^3$ configuration, so in hydrogenic terms we would expect the lowest states to be $1s^2 2s$ and $1s^2 2p$. In *H*, $2s$ and $2p$ are degenerate, so how can we distinguish here? Expect $1s^2 2s$ to be lowest, since electron in $2s$ state "spends more time" close to the nucleus.¹ Careful of this argument: might make it in *H* also, would be wrong. Point is that in *Li*, when "valence" ($n=2$) electron spends time near nucleus, so is (some of the time) inside core of $1s$ electrons, so feels full nuclear charge $q_{eff} \simeq +3$, instead of partially "screened" charge $q_{eff} \simeq +1$; lowers Coulomb energy considerably.

Note 2 electrons in $1s^2$ state are in same spatial state, so Pauli forces them to be in spin singlet (antisymmetric) state, i.e. $S = 0$. So expect (although classification based on *H*-orbitals not exact!) that the spin of both $1s^2 2s$ ground state and $1s^2 2p$ excited state will be $1/2$ due to extra e^- . So spectroscopic "terms" $^S L$ for these states are $^2 S$ and $^2 P$.

Here's full picture from spectroscopy:

Because $2s$ wave fctn $\propto (1 - r/2a_0)e^{-r/2a_0}$ instead of e^{-r/a_0} , it spends much more time at larger radii than core electrons. Can view *Li* ground state as *He* "core" with one rather loosely bound electron on top.

I won't dwell on the rest of periodic table in these lectures. See Gasiorowicz

¹Because p wave function is odd parity, hence zero at origin.

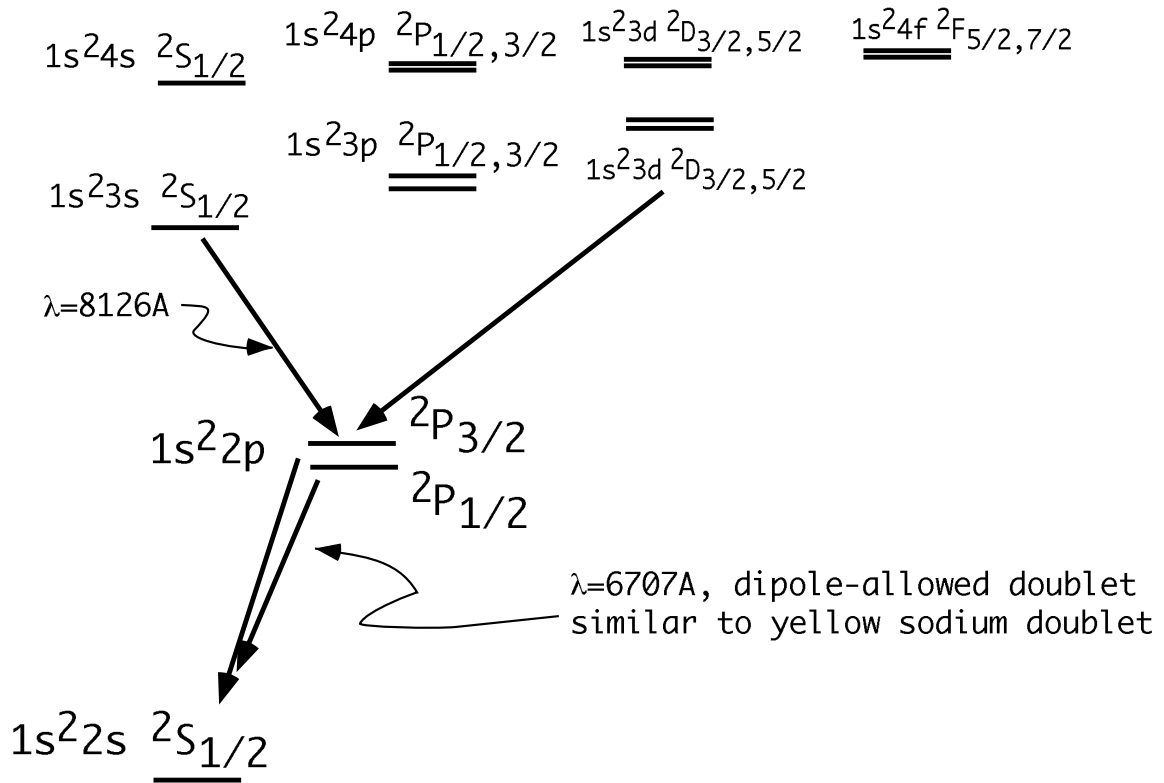


Figure 1: Low-lying *Li* levels and transitions.

for more systematic discussion.

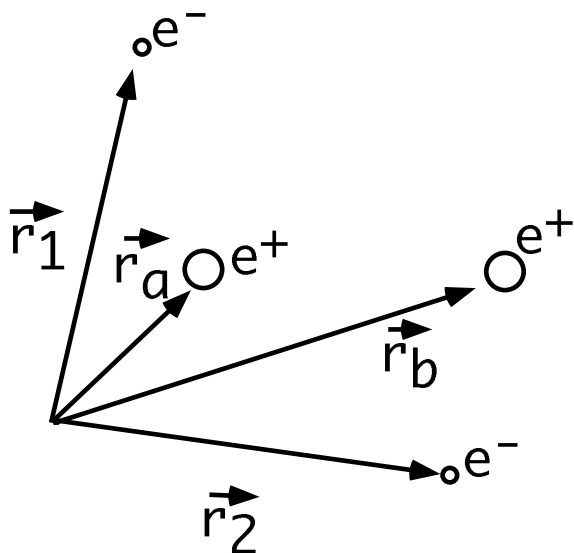
7.2 Hydrogen molecule

Although there are 2 protons and two electrons as in *He*, *H₂* molecule is different problem because lack of single center of symmetry. Take protons at positions \mathbf{r}_a and \mathbf{r}_b . Full Hamiltonian is

$$H = H_0 + H_1, \quad (1)$$

$$H_0 = \frac{\hat{p}_1^2}{2m_e} + \frac{\hat{p}_2^2}{2m_e} - \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_a|} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{r}_b|} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{r}_a|} - \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_b|} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{e^2}{|\mathbf{r}_a - \mathbf{r}_b|}, \quad (2)$$

$$H_1 = \frac{\hat{p}_a^2}{2m_p} + \frac{\hat{p}_b^2}{2m_p} \quad (3)$$



Questions:

1. How far apart do the protons prefer to sit, and why is the molecule stable?
2. What are vibrational and rotational modes of molecule, & how do they correspond to simple-minded “rotating dumbbell” picture?

Born-Oppenheimer approximation

Idea is to use the fact that protons are much heavier and slower than the electrons.

1. Imagine 1st that they are *fixed* at \mathbf{r}_a and \mathbf{r}_b . Then $H_1 \rightarrow 0$, and note soln to $H_0\phi = E^{(0)}\phi$ is some fctn. depending only on the coords. of electrons relative to protons:² $\phi(\mathbf{r}_a - \mathbf{r}_b, \mathbf{r}_1 - \mathbf{r}_a, \mathbf{r}_2 - \mathbf{r}_a)$
2. Suppose we had such soln. 2nd step is to seek approx. soln. to full S.-eqn. $H\Psi = E\Psi$ of form

$$\Psi(\mathbf{r}_a, \mathbf{r}_b) = \psi(\mathbf{r}_a, \mathbf{r}_b)\phi \quad (4)$$

Effectively ψ can be thought of as the proton wave fctn., and ϕ the

²and not on \mathbf{r}_a and \mathbf{r}_b independently.

electron wave fctn.³ ψ contains info not only on the relative motion of protons, but also center of mass translation of molecule!

Now note that

$$H_1\Psi = \phi H_1\psi + \psi H_1\phi - \frac{\hbar^2}{m_p} (\nabla_a\phi \cdot \nabla_a\psi + \nabla_b\phi \cdot \nabla_b\psi) \quad (5)$$

$$\simeq \phi H_1\psi \quad (6)$$

where last major simplification results from fact that derivatives of proton wave fctn. wrt proton coords. are much larger than those of electron wave fctn. wrt proton coords.,

$$|\nabla_a\phi\nabla_a\psi| \ll |\phi\nabla_a^2\psi| \quad (7)$$

This follows from fact that proton ψ must “wiggle” more rapidly than electron ϕ since $m_e \ll m_p$.⁴ Full S.-eqn. is now approx.

$$H(\psi\phi) = \psi H_0\phi + \phi H_1\psi \quad (8)$$

$$= \phi E^{(0)}\phi + \phi H_1\psi \quad (9)$$

$$= \phi(H_1 + E^{(0)})\psi = E\psi\phi \quad (10)$$

As we expect, factorizing wave fctn. decouples S.-eqn. so we get eqn. for nuclear coords. alone, by cancelling ϕ :

$$(H_1 + E^{(0)}(r))\psi = E\psi \quad (11)$$

where $r = |\mathbf{r}_a - \mathbf{r}_b|$, and $E^{(0)}$ may be written as fctn of r alone since we supposedly kept r fixed to solve the ϕ -eqn.

³It is our assumption of *statistical independence* of the electronic and nuclear degrees of freedom which leads to factorizable wavefctn—remember the problem with two independent pieces of the Hamiltonian? Of course the exact Ψ will not factorize this way, to the extent the motion of the electrons and the motion of the nuclei are correlated.

⁴Typical length scale in proton wave fctn, roughly equal to Bohr radius for proton, mass m_p , charge e moving in Coulomb field of another charge e , i.e. $a_0^p \simeq \hbar^2/m_p e^2$. This is much *smaller* than the usual Bohr radius $a_0 = \hbar^2/m_e e^2$ which sets scale for electron wave function spatial variation.

3. Now we've formulated problem for nuclei in terms of an effective potential $E^{(0)}(r)$ due to electrons. If we do it correctly, this potential should have minimum for some r_0 , which is relative distance protons like to sit wrt each other.

Find effective potential: solve $H_0\phi = E^{(0)}(r)\phi$:

Classify solns. according to eigenvalue under reflection about axis joining protons, $\mathbf{r}_a \leftrightarrow \mathbf{r}_b$. Traditional to use German designations g ("gerade") for even and u ("ungerade") for odd. Although H_0 isn't rotationally symmetric, it is symmetric wrt rotations around axis connecting protons, so should be able to classify eigenstates of H_0 according to their total \hat{L}_z along this axis. These are given "molecular orbital" designation

$$\begin{aligned} \Sigma & m = 0 \\ \Pi & m = 1 \\ \Delta & m = 2 \end{aligned} \tag{12}$$

Focus on 2 lowest Σ states, spin singlet $^1\Sigma_g$ and triplet $^3\Sigma_u$. Just as for He atom, construct trial wave fctn. using hydrogenic orbitals:⁵

$$\psi_u^g = (u_{1s}(\mathbf{r}_1 - \mathbf{r}_a)u_{1s}(\mathbf{r}_2 - \mathbf{r}_b) \pm u_{1s}(\mathbf{r}_1 - \mathbf{r}_b)u_{1s}(\mathbf{r}_2 - \mathbf{r}_a)) \begin{cases} |00\rangle \\ |1M_s\rangle \end{cases} \tag{13}$$

where $+$ sgn gives symm. space, antisym. spin wave fctn, $-$ sgn opposite. The u_{1s} are hydrogenic s-wave states, $u_{1s} \sim e^{-\alpha r}$.

What we should do is use the variational principle to calculate

$$E_{u}^{g(0),var} \equiv \frac{\langle \psi_u^g | H_0 | \psi_u^g \rangle}{\langle \psi_u^g | \psi_u^g \rangle} \geq E_u^{g(0)} \tag{14}$$

using (13). This is straightforward but an order of magnitude more tedious than even He .⁶ So I'll just sketch numerical result:

Physical intuition why $^1\Sigma_g$ is lowest (superscript is $2S + 1$ as usual): spatial fctn. *symmetric* under $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$, meaning electron density large in between two sites (see fig 3B), has two consequences:

⁵Note that these particular fctns. are also even/odd under the operation $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$, but this is a separate symmetry. As far as I have been able to determine, g and u refer to eigenvalue under exchange of protons a and b . See discussion of excited states.

⁶For a nice treatment, see Gasiorowicz, *Quantum Physics*, New York: Wiley, 1996, pp. 324-331.

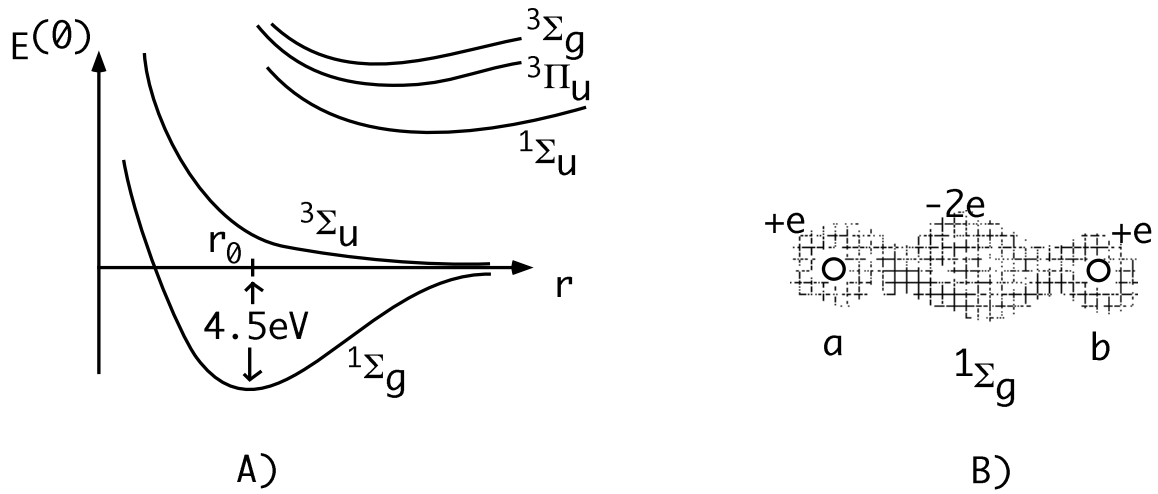


Figure 2: A) Effective nuclear potential $E^{(0)}(r)$; B) Chemical bond formation in $^1\Sigma_g$ state.

1. $\langle e^2/r_{12} \rangle$ increases
2. $\langle -e^2/|\mathbf{r}_1 - \mathbf{r}_a| \rangle$, etc. decreases

Turns out 2nd effect wins, leading to potential minimum in singlet $^1\Sigma_g$ state at around $r_0 = 0.742A$ (see fig 3A). By contrast in triplet state $^3\Sigma_u$, prob. of finding 2 electrons at $\mathbf{r}_1 = \mathbf{r}_2$ is zero, so sign of 2 effects is reversed, leading to no minimum in $E^{(0)}(r)$. Molecule is not stable in this state.⁷ Weak maxima *are* found for other configurations e.g. $1s2s$ and $1s2p \implies$ metastable states.

Right now I don't see a compelling heuristic argument which says why effect 2) wins over effect 1) above. But take note of this small energy reduction of the singlet relative to the triplet: it is a vitally important quantum mechanical effect called *exchange*, and can be estimated in the trial wave fctn. we have been using. Want to calculate energy

$$E_g^{(0),var} = \langle \psi_g^u | H_0 | \psi_g^u \rangle \quad (15)$$

$$= 2E_1 + e^2 \int d^3r_1 d^3r_2 \psi_g^u(\mathbf{r}_1, \mathbf{r}_2) \left(\frac{1}{r} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_b|} - \frac{1}{|\mathbf{r}_2 - \mathbf{r}_a|} \right) \psi_g^u(\mathbf{r}_1, \mathbf{r}_2) \quad (16)$$

where $\psi_g^u(\mathbf{r}_1, \mathbf{r}_2)$ given by (13) and E_1 is -1Ryd, ground st. energy of H atom. $2E_1$ term comes from splitting off the terms in H_0 which correspond to independent H -atoms for $(e^{-1}, p a)$ and $(e^{-2}, p b)$. Rewrite, separating out direct terms and cross terms:

$$E_g^{(0),var} = 2E_1 + \frac{e^2}{r} + a_g^u (V_C(r) \pm V_{ex}(r)) \quad (17)$$

where a_g are normalization const. for (13). Introduce shorthand $u_{1s}^a(1) \equiv u_{1s}(\mathbf{r}_1 - \mathbf{r}_a)$, etc. Then *Coulomb integral* and *exchange integral* are defined to be

⁷stable state is called *bonding* molecular orbital, unstable one *antibonding* according to how much time the 2 electrons spend near each other in along the "bond" between the two nuclei.

$$V_C(r) = \int d^3r_1 d^3r_2 |u_a(1)|^2 |u_b(2)|^2 \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_b|} - \frac{1}{|\mathbf{r}_2 - \mathbf{r}_a|} \right) \quad (18)$$

$$V_{ex}(r) = \int d^3r_1 d^3r_2 u_a^*(1) u_b^*(2) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_b|} - \frac{1}{|\mathbf{r}_2 - \mathbf{r}_a|} \right) u_a(2) u_b(1) \quad (19)$$

Note integrand in (19) peaks up only when electrons 1 and 2 spends some time *between a and b*, hence term *exchange*.

Find nuclear motion in effective potential of grnd. state $^1\Sigma_g$

To find low-lying vibrational states of H_2 molecule, we can now use what we've learned about the effective potential. Consider small oscillations about pot. minimum, then quantize them:

$$E^{(0)}(r) \simeq E^{(0)}(r_0) + \frac{1}{2}k(r - r_0)^2, \quad (20)$$

variational calculation yields $k = 35.2\text{eV}/\text{\AA}^2$. Natural osc. freq. is then

$$\omega_0 = \sqrt{\frac{k}{\mu}} = \sqrt{\frac{2k}{m_p}} \quad (21)$$

where μ is 2-body reduced mass, $\mu = m_p/2$. So spectrum of vibrational states we expect to look like 1D SHO (motion is in 1D along axis betw. protons),

$$E_n = E^{(0)}(r_0) + \hbar \sqrt{\frac{2k}{m_p}} \left(n + \frac{1}{2} \right) \quad (22)$$

Other "terms" in H_2

Reexamine meaning of wave fctns. of low-lying Σ states (13). In our shorthand notation, (13) is

$$\psi_u^g = (u_{1s}^a(1)u_{1s}^b(2) \pm u_{1s}^b(1)u_{1s}^a(2)) \begin{cases} \chi^{sing} \\ \chi^{trip} \end{cases} \quad (23)$$

Recall all fctns decay exponentially as args. get large. Ask when can ψ be large if I separate protons to great distance, i.e. $r = |\mathbf{r}_a - \mathbf{r}_b| \rightarrow \infty$? For fctns. (23) see that, e.g. if electron 1 near proton a , and electron 2 near proton b , 1st term can be of order 1.⁸ So these states describe 2 neutral

⁸2nd term falls away, which explains why the two lowest states approach each other for large r in Fig. 2

H atoms at large distances. Other types of states possible, however. Look at combinations

$$\psi_g = (u_{1s}^a(1)u_{1s}^a(2) \pm u_{1s}^b(1)u_{1s}^b(2))\chi_{sing} \quad (24)$$

Note *both* states in (24) *even* under interchange of $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$, hence must have $S = 0$, yet the minus (plus) sign in (24) gives a state *ungerade*/odd (*gerade*/even) under $\mathbf{r}_a \leftrightarrow \mathbf{r}_b$. So these give two new terms just from hydrogenic $1s$ orbitals, ${}^1\Sigma_u$ and ${}^1\Sigma_g$. The ${}^1\Sigma_u$ term is relatively low in energy. To estimate, look at large r behavior.

Since these involve products of type $u^a(1)u^a(2)$, only way wave fctn. can remain large as $r \rightarrow \infty$ is if both electron 1 *and* electron 2 stay on, e.g., proton a . In other words, these states correspond to hydrogen ions H^- weakly bound to a proton—what chemists call *ionic bond*. Binding energy of 2nd e^- on H^- is $\sim 0.7\text{eV}$, so at large r binding energy should go to $13.6 - 0.7 \text{ eV} \simeq 12.9 \text{ eV}$ above large- r limits of lowest states.

Can construct higher states by using higher hydrogenic orbitals, e.g. u_{2s} . Define

$$A \quad u_{1s}^a(1)u_{2s}^b(2) \quad (25)$$

$$B \quad u_{1s}^b(1)u_{2s}^a(2) \quad (26)$$

$$C \quad u_{1s}^a(2)u_{2s}^b(1) \quad (27)$$

$$D \quad u_{1s}^b(2)u_{2s}^a(1) \quad (28)$$

giving possible combinations and terms

$$A + B + C + D \quad {}^1\Sigma_g \quad (29)$$

$$A + B - C - D \quad {}^3\Sigma_g \quad (30)$$

$$A - B + C - D \quad {}^1\Sigma_u \quad (31)$$

$$A - B - C + D \quad {}^3\Sigma_u \quad (32)$$

Check to make sure you understand just by looking at properties of combinations (29-32) under both exchanges why the term symbols are determined as shown.

Finally, we could also choose a (nearly degenerate) $2p$ wave fctn. to combine with the $1s$:

$$A' \quad u_{1s}^a(1)u_{2p}^b(2) \quad (33)$$

$$B' \quad u_{1s}^b(1)u_{2p}^a(2) \quad (34)$$

$$C' \quad u_{1s}^a(2)u_{2p}^b(1) \quad (35)$$

$$D' \quad u_{1s}^b(2)u_{2p}^a(1) \quad (36)$$

Now we apply same argument under two exchanges as for s -orbitals, except note $2p$ orbital negative under reflection of space about midpoint between 2 nuclei, so one add'l minus sign, i.e. under $\mathbf{r}_a \leftrightarrow \mathbf{r}_b$. Possible combinations and terms:

$$A' + B' + C' + D' \quad {}^1\Pi_u \quad (37)$$

$$A' + B' - C' - D' \quad {}^3\Pi_u \quad (38)$$

$$A' - B' + C' - D' \quad {}^1\Pi_g \quad (39)$$

$$A' - B' - C' + D' \quad {}^3\Pi_g \quad (40)$$

Lowest lying combinations of this type appear to be (30) and (38) (Fig. 3).