

Physics 531, Problem Set #3

Solutions

Problem 1: Perturbation calculation

We consider a configuration $(1s)(2p)$ of a Helium-like atom of nuclear charge Ze , approximating each orbital as hydrogenic $(1s)$ with nucleus Ze , $(2p)$ with nucleus $(Z-1)e$.

(a) We consider the matrix element

$$\langle \phi_A(1) \phi_B(2) | \frac{1}{r_{12}} | \phi_C(1) \phi_D(2) \rangle$$

where the ϕ 's are: $\phi_{nlm}(\vec{r}) = \frac{u_{nl}(r)}{r} Y_{lm}(\theta, \phi)$

with $u_{nl}(r)$ the (reduced) radial wave function of a hydrogen state with some nuclear charge

We use the "addition theorem"

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{(r_<)^l}{(r_>^{l+1})} \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_{l,m}^*(\theta_1, \phi_1) Y_{l,m}(\theta_2, \phi_2)$$

where $r_<(r_>)$ is the lesser (greater) of

r_1 or r_2

$$\Rightarrow \langle \phi_A^{(1)} \phi_B^{(2)} | \frac{1}{r_{12}} | \phi_C^{(1)} \phi_D^{(2)} \rangle$$

$$= \sum_l \frac{4\pi}{2l+1} \int_0^\infty dr_1 \int_0^\infty dr_2 \frac{(r_1)^l}{(r_2)^{l+1}} u_A^{(1)} u_C^{(1)} u_B^{(2)} u_D^{(2)}$$

$$\sum_m \int d\Omega_1 Y_{l, m_A}^*(\theta_1, \phi_1) Y_{l, m}^*(\theta_1, \phi_1) Y_{l, m_C}(\theta_1, \phi_1)$$

$$\int d\Omega_2 Y_{l, m_B}^*(\theta_2, \phi_2) Y_{l, m}(\theta_2, \phi_2) Y_{l, m_D}(\theta_2, \phi_2)$$

By the rules of the integrals of 3 $Y_{l, m}$'s the above integral vanishes, unless

$$m_B = m + m_D$$

$$m_C = m + m_A$$

$$\Rightarrow m_B - m_D = m_C - m_A$$

$$\Rightarrow \boxed{m_A + m_B = m_C + m_D}$$

thus

$$\langle \phi_A^{(1)} \phi_B^{(2)} | \frac{1}{r_{12}} | \phi_C^{(1)} \phi_D^{(2)} \rangle$$

$$= \sum_{m_A + m_B, m_C + m_D} \sum_k C_{l_A m_A, l_C m_C}^{(k)} C_{l_B m_B, l_D m_D}^{(k)} \frac{4\pi}{2k+1}$$

$$F^{(k)}(AB, CD)$$

where
$$C_{lm, l'm'}^{(k)} \equiv \int d\Omega Y_{lm}^*(\theta, \phi) Y_{k, m-m'}(\theta, \phi) Y_{l', m'}$$

$$= C_{lm, l', m'}^{(k)*} \quad (\text{real})$$

$$F_{(A, B, C, D)}^{(k)} \equiv \int dr_1 dr_2 \frac{r_2^k}{r_1^{k+1}} u_A(1) u_C(1) u_B(2) u_D(2)$$

(b) The two terms arising from the (2s)(2p) config

$${}^1P_{(m_x)} = \frac{1}{\sqrt{2}} \left\{ \phi_{1s}^{(2)}(1) \phi_{2p, m_x}^{(2-1)}(2) + \phi_{2p, m_x}^{(2-1)}(1) \phi_{2s}^{(2)}(2) \right\} \chi_0^{\text{singlet}}$$

$${}^3P_{(m_x, m_s)} = \frac{1}{\sqrt{2}} \left\{ \phi_{1s}^{(2)}(1) \phi_{2p, m_x}^{(2-1)}(2) - \phi_{2p, m_x}^{(2-1)}(1) \phi_{2s}^{(2)}(2) \right\} \chi_{m_s}^{\text{Triplet}}$$

Note: I have denoted these states with m_s, m_x quantum numbers, though if the absence of external fields the energy does not depend on them, and they may be chosen arbitrarily.

I will pick $m_x = 0$

$$\Rightarrow \phi_{1s}^{(2)}(r) = \frac{2Z^{3/2}}{\sqrt{4\pi}} e^{-2r}$$

$$\phi_{2p, 0}^{(2-1)}(r, \theta) = \frac{(Z-1)^{5/2}}{2\sqrt{6}} r e^{-\frac{(Z-1)}{2}r} \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$R_{2p}^{(2-1)}(r)$$

$$Y_{1,0}(\theta)$$

The total Hamiltonian is (in atomic units)

$$H = -\frac{1}{2} \nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

The energy to first order is the expectation value

$$E = \langle \psi_{\pm} | H | \psi_{\pm} \rangle = \langle \psi_{\pm} | H_0^{(1)} | \psi_{\pm} \rangle + \langle \psi_{\pm} | H_0^{(2)} | \psi_{\pm} \rangle + \langle \psi_{\pm} | \frac{1}{r_{12}} | \psi_{\pm} \rangle$$

where $|\psi_{\pm}\rangle \stackrel{\text{singlet}}{\underset{\text{triplet}}{=}} \frac{1}{\sqrt{2}} (\phi_{1s}^{(2)}(1) \phi_{2p,0}^{(z-1)}(2) \pm \phi_{2p,0}^{(z)}(1) \phi_{1s}^{(z)}(2))$

(Where $H_0^{(i)} = \frac{1}{2} \nabla_i^2 - \frac{Z}{r_i}$ is the Hydrogenic Hamiltonian)

Following Lect. 11 note

$$\begin{aligned} \langle \psi_{\pm} | H_0 | \psi_{\pm} \rangle &= \frac{1}{2} \left(\langle \phi_{1s}^{(2)}(1) | H_0^{(1)} | \phi_{1s}^{(2)}(1) \rangle + \langle \phi_{1s}^{(z)}(2) | H_0^{(2)} | \phi_{1s}^{(z)}(2) \rangle \right) \\ &\quad + \frac{1}{2} \left(\langle \phi_{2p}^{(z-1)}(1) | H_0^{(1)} | \phi_{2p}^{(z-1)}(1) \rangle + \langle \phi_{2p}^{(z)}(2) | H_0^{(2)} | \phi_{2p}^{(z)}(2) \rangle \right) \\ &= \underbrace{\langle \phi_{1s}^{(z)} | H_0 | \phi_{1s}^{(z)} \rangle}_{E_0^{(z)}(1s,z)} + \underbrace{\langle \phi_{2p}^{(z-1)} | H_0 | \phi_{2p}^{(z-1)} \rangle}_{E_0^{(z)}(2p,z-1)} \end{aligned}$$

The first term is just the Hydrogenic energy for one electron in a nucleus of charge Z

$$E_0^{(z)}(1s,z) = -\frac{Z^2}{2}$$

To calculate $E_0^{(z)}(2p, z-1)$ we use the Virial theorem as in Lecture 11

$$\langle \phi_{2p}^{(z-1)} | H_0^{(z)} | \phi_{2p}^{(z-1)} \rangle = \langle \phi_{2p}^{(z-1)} | \frac{1}{2} \nabla^2 | \phi_{2p}^{(z-1)} \rangle + \langle \phi_{2p}^{(z-1)} | -\frac{z}{r} | \phi_{2p}^{(z-1)} \rangle$$

By Virial $\langle KE \rangle = -E_{2p}^{(z-1)} = \frac{+(z-1)^2}{8}$

$$\langle PE \rangle = +\frac{z}{(z-1)} \underbrace{\langle \phi_{2p}^{(z-1)} | \frac{(z-1)}{r} | \phi_{2p}^{(z-1)} \rangle}_{2E_{2p}^{(z-1)} = \frac{2-(z-1)^2}{2(z)^2}} = -\frac{z(z-1)}{4}$$

Thus,

$$\langle H \rangle_{\pm} = -\frac{z^2}{2} + \frac{(z-1)^2}{8} - \frac{z(z-1)}{4} + \left\langle \frac{1}{r_{12}} \right\rangle_{\pm}$$

The first term is the $\text{He}^+(1s)$ binding energy. The energy of the state relative to the first ionization threshold is

$$E_{\pm} = \frac{(z-1)^2}{8} - \frac{z(z-1)}{4} + \left\langle \frac{1}{r_{12}} \right\rangle_{\pm} \quad (\text{au})$$

$$\text{Now } \left\langle \frac{1}{r_{12}} \right\rangle_{\pm} = \underbrace{\left\langle \phi_{1s}^{(z)} \phi_{2p}^{(z-1)} \left| \frac{1}{r_{12}} \right| \phi_{1s}^{(z)} \phi_{2p}^{(z-1)} \right\rangle}_{\equiv F \text{ (direct)}} + \underbrace{\left\langle \phi_{1s}^{(z)} \phi_{2p}^{(z-1)} \left| \frac{1}{r_{12}} \right| \phi_{1s}^{(z-1)} \phi_{2p}^{(z)} \right\rangle}_{\equiv G \text{ (exchange)}}$$

From Part (a)

$$F = \sum_k \frac{4\pi}{k} \int dr_1 dr_2 \frac{r_2^k}{r_1^{k+1}} |u_{1s}^{(z)}(r_1)|^2 |u_{2p}^{(z-1)}(r_2)|^2 \int d\Omega Y_{00}^* Y_{k0} Y_{00} \int d\Omega Y_{10}^* Y_{k0} Y_{10}$$

Only one k value satisfies the triangle inequality, $k=0$
 $Y_{00} = \frac{1}{\sqrt{4\pi}}$

$$\begin{aligned} \Rightarrow F &= \int dr_1 dr_2 \frac{1}{r_1} |u_{1s}^{(z)}(r_1)|^2 |u_{2p}^{(z-1)}(r_2)|^2 \\ &= \frac{z^3 (z-1)^5}{6} \int dr_1 \int dr_2 \frac{1}{r_1} r_1^2 e^{-2zr_1} r_2^4 e^{-(z-1)r_2} \\ &= \frac{z^3 (z-1)^5}{6} \int_0^\infty dr_2 r_2^4 e^{-(z-1)r_2} \left\{ \frac{1}{r_2} \int_0^{r_2} dr_1 r_1^2 e^{-2zr_1} + \int_{r_2}^\infty dr_1 r_1 e^{-2zr_1} \right\} \\ &\quad \left\{ \frac{1}{4z^3 r_2} (1 - e^{-2zr_2}) - \frac{1}{4z^2} e^{-2zr_2} \right\} \\ &= \frac{(z-1)^5}{24} \int_0^\infty dr \left(r^3 (e^{-(z-1)r} - e^{-(3z-1)r}) - z r^4 e^{-(3z-1)r} \right) \end{aligned}$$

$$\Rightarrow F = \frac{z-1}{4} - \frac{(z-1)^5}{4(3z-1)^4} - \frac{z(z-1)^5}{(3z-1)^5} = \frac{z-1}{4} - \frac{(z-1)^5(7z-1)}{4(3z-1)^5}$$

The exchange term

$$G = \left\langle \phi_{1s}^{(z)}(1) \phi_{2p}^{(z-1)}(2) \left| \frac{1}{r_{12}} \right| \phi_{2p}^{(z-1)}(1) \phi_{1s}^{(z)}(2) \right\rangle$$

$$= \sum_k \frac{4\pi}{2k+1} \int d\Omega_1 d\Omega_2 u_{1s}(r_1) u_{2p}(r_2) u_{1s}(r_2) u_{2p}(r_1)$$

$$\int d\Omega_1 Y_{00}^*(1) Y_{k0}(1) Y_{10}(1)$$

$$\int d\Omega_2 Y_{00}^*(2) Y_{k0}(2) Y_{00}(2)$$

Here only $k=1$, each angular integral = $\frac{1}{\sqrt{4\pi}}$

$$\Rightarrow G = \frac{z^3(z-1)^5}{18} \int_0^\infty dr_1 r_1^3 e^{-(3z-1)r_1/2} \int_0^\infty dr_2 \frac{r_2}{r_2^2} r_2^3 e^{-(3z-1)r_2/2}$$

by symmetry = $\frac{2z^3(z-1)^5}{18} \int_0^\infty dr r^4 e^{-(3z-1)r/2} \int_{r'}^\infty dr' r' e^{-(3z-1)r'/2}$

$$= \frac{2z^3(z-1)^5}{18} \int_0^\infty dr r^4 e^{-(3z-1)r/2} \left(\frac{2r}{3z-1} + \frac{4}{(3z-1)^2} \right) e^{-(3z-1)r/2}$$

$$\Rightarrow G = \frac{112}{3} \frac{z^3(z-1)^5}{(3z-1)^7}$$

$$\therefore E_{\pm} = -\frac{(z+1)^2}{8} - \frac{(z-1)^5}{4(3z-1)^5} (7z-1) \pm \frac{112}{3} \frac{z^3(z-1)^5}{(3z-1)^7}$$

For He $Z=2$, $1 \text{ Hartree} = 2.1947 \times 10^5 \text{ cm}^{-1}$

$$E_+ = E_{1p} = -0.1222 \text{ au} = -26,819 \text{ cm}^{-1} \text{ for } 1p$$

$$E_- = E_{3p} = -0.1299 \text{ au} = -28,509 \text{ cm}^{-1} \text{ for } 3p$$

OK agreement $\sim 1\% - 2\%$ of level energies
 $10 - 20\%$ of splitting

(c) The splitting is twice the exchange interaction



$$\Delta E = 2G = \frac{224}{3} \frac{Z^3}{(3Z-1)^2} \approx 2.195 \times 10^5 \text{ cm}^{-1} / \text{au}$$

Atom	$^2P_1/2$ (cm $^{-1}$)	$\langle ^3P_J \rangle$ cm $^{-1}$	ΔE_{expt} (cm $^{-1}$)	ΔE_{theory} (cm $^{-1}$)
He I	171,135	169,086	2047	1,690
Li II	501,809	499,266	7542	6,752
Be III	997,454	983,366	14,084	13,077
B IV	1,657,480	1,636,938	21,005	19,901
C V	3,483,372	3,455,169	28,080	26,960
N VI	3,973,790	3,938,320	35,180	34,151
O VII	4,629,201	4,585,680	42,971	41,921
F VIII	5,949,900	5,900,750	49,150	48,745

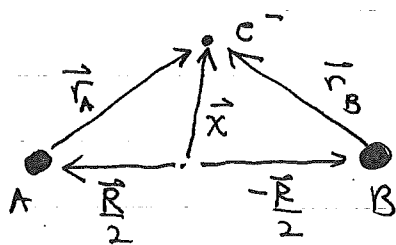
Better agreement as $Z \rightarrow \infty$

Error due to single particle orbital choice

Problem Set #3 Solutions

Problem 2: Diatomic Molecule

(a) H_2^+ molecule in the B-O approximation



- Two fixed protons.
- Electrons move very fast
- ⇒ Eigenstates parametrized by R

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m} - \frac{e^2}{\hat{r}_A} - \frac{e^2}{\hat{r}_B}}_{\hat{H}'}} + \underbrace{\frac{e^2}{R}}_{\text{Not operator}}$$

- Nuclei move slowly and electrons adiabatically follow

Trial ground-state wave function for electron

$$\tilde{\Psi}(\vec{x}) = c_A \psi_A(\vec{x}) + c_B \psi_B(\vec{x})$$

where $\psi_{A(B)}(\vec{x}) = \phi_{1s}(\vec{x} \mp \frac{\vec{R}}{2}) = \phi_{1s}(\frac{\vec{R}}{2})_{A(B)}$

with $\phi_{1s}(\vec{x}) = \frac{1}{\sqrt{\pi}a_0^3} e^{-|\vec{x}|/a_0}$ (The 1s Hydrogen orbital)

Variational energy

$$\bar{E}(c_A, c_B) = \frac{\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle}$$

(Next Page)

$$\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = c_A^2 \langle \psi_A | \hat{H}' | \psi_A \rangle + c_B^2 \langle \psi_B | \hat{H}' | \psi_B \rangle$$

$$+ 2c_A c_B \langle \psi_B | \hat{H}' | \psi_A \rangle + \frac{e^2}{R} \langle \tilde{\Psi} | \tilde{\Psi} \rangle$$

(where I have used c_A, c_B real; $\psi_A(\vec{x}), \psi_B(\vec{x})$ real)

Aside: $\langle \psi_A | \hat{H}' | \psi_A \rangle = \langle \psi_A | \left(\frac{\hat{p}^2}{2m} - \frac{e^2}{r_A} \right) | \psi_A \rangle + \langle \psi_A | -\frac{e^2}{r_B} | \psi_A \rangle$

$$\langle \psi_B | \hat{H}' | \psi_B \rangle = \langle \psi_B | \left(\frac{\hat{p}^2}{2m} - \frac{e^2}{r_B} \right) | \psi_B \rangle + \langle \psi_B | -\frac{e^2}{r_A} | \psi_B \rangle$$

Using the symmetry of the problem, we see that

- $\langle \psi_A | \frac{\hat{p}^2}{2m} - \frac{e^2}{r_A} | \psi_A \rangle = \langle \psi_B | \frac{\hat{p}^2}{2m} - \frac{e^2}{r_A} | \psi_B \rangle = E_{H^{(1)}} = -13.6 \text{ eV}$
- $\langle \psi_A | -\frac{e^2}{r_B} | \psi_A \rangle = \langle \psi_B | -\frac{e^2}{r_A} | \psi_B \rangle \equiv I$ ("Coulomb integral")

(Given $I = \int d^3x |\psi_A(\vec{x})|^2 \left(-\frac{e^2}{r_B} \right) = \frac{e^2}{a_0} \left(-\frac{1}{R} + e^{-2R} \left(1 + \frac{1}{R} \right) \right)$
($R \equiv R/a_0$))

Aside: $\langle \psi_B | \hat{H}' | \psi_A \rangle = \langle \psi_B | \underbrace{\left(\frac{\hat{p}^2}{2m} - \frac{e^2}{r_A} \right)}_{\text{Eigenstate } E_{H^{(1)}} | \psi_A \rangle} | \psi_A \rangle + \langle \psi_B | -\frac{e^2}{r_B} | \psi_A \rangle$

$$= E_{H^{(1)}} P_{AB} + M$$

where $P_{AB} = \langle \psi_B | \psi_A \rangle = e^{-R} \left(1 + R + \frac{R^2}{3} \right)$

$$M = \langle \psi_B | -\frac{e^2}{r_B} | \psi_A \rangle = \int d^3x \psi_B(\vec{x}) \left(-\frac{e}{r_B} \right) \psi_A(\vec{x})$$

$$= -\frac{e^2}{a_0} e^{-R} (1 + R) \quad (\text{"Resonance integral"})$$

Finally $\langle \tilde{\Psi} | \tilde{\Psi} \rangle = c_A^2 + c_B^2 + 2c_A c_B P_{AB}$

Thus the variational energy is

$$\bar{E}(c_A, c_B) = \frac{(E_H^{(1s)}(c_A^2 + c_B^2 + 2c_A c_B P_{AB}) + (c_A^2 + c_B^2)I + 2c_A c_B M) + \frac{e^2}{R} \langle \tilde{\Psi} | \tilde{\Psi} \rangle}{c_A^2 + c_B^2 + 2c_A c_B P_{AB}}$$

$$\Rightarrow \bar{E}(c_A, c_B) = E_H^{(1s)} + \frac{(c_A^2 + c_B^2)I + 2c_A c_B M}{c_A^2 + c_B^2 + 2c_A c_B P_{AB}} + \frac{e^2}{R}$$

Now we must minimize w.r.t. the parameters c_A and c_B . We seek the solutions to

$$\frac{\partial \bar{E}}{\partial c_A} = \frac{\partial \bar{E}}{\partial c_B} = 0$$

After some algebra:

$$\Rightarrow \frac{2c_B(c_A^2 - c_B^2)(I P_{AB} - M)}{(c_A^2 + c_B^2 + 2c_A c_B P_{AB})^2} = 0 = \frac{-2c_A(c_A^2 - c_B^2)(I P_{AB} - M)}{(c_A^2 + c_B^2 + 2c_A c_B P_{AB})^2}$$

Since $I < 0$ $M < 0$ $P_{AB} > 0$ and both c_A and $c_B \neq 0$

$$\Rightarrow c_A^2 - c_B^2 = 0$$

$$\Rightarrow \boxed{c_A = \pm c_B} \quad \text{To minimize energy}$$

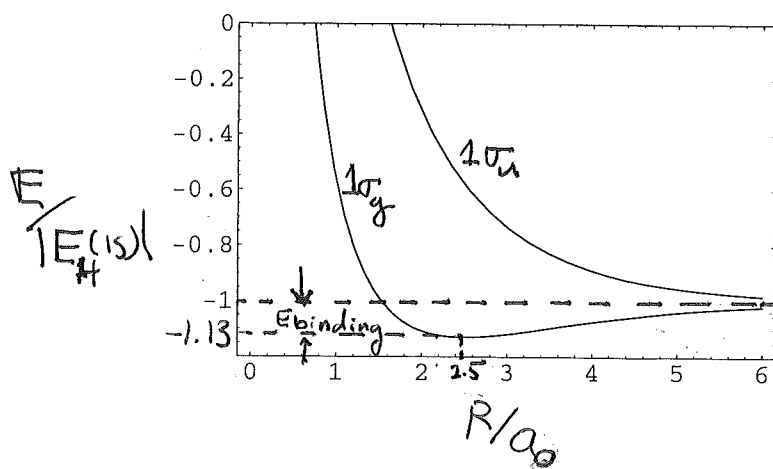
Thus, the variational solution for the ground state energy involve symmetric and antisymmetric combination of the atomic orbitals (as we could have guessed). These correspond to the "gerade" and "ungerade" solutions for the electron parity:

$$|1\sigma_{g(u)}\rangle = |\psi_A\rangle \pm |\psi_B\rangle \quad (\text{unnormalized})$$

$$E(1\sigma_{g(u)}) = E_H(1s) + \frac{I \pm M}{1 \pm P_{AB}} + \frac{e^2}{R}$$

Here the electron wave function is denoted as a "molecular orbital" $|l_z|_p \leftarrow \text{parity}$ ($\sigma \rightarrow l_z = 0$)
 \uparrow
 angular momentum about internuclear axis

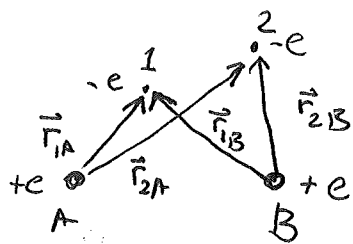
(b) Plugging in the R dependence for the Coulomb and resonance integral we arrive at the B-O potential for the nuclei.



We see that the $1\sigma_g$ state provides a shallow binding potential for the nuclei

- Equilibrium separation $2.5 a_0$
- Binding energy $0.13 |E_H(1s)| = 1.76 \text{ eV}$

(C) Neutral H_2 in B-O approximation



Two electrons in the field of two protons

Again we take the nuclei as fixed on the time scale that the electrons move.

$$\hat{H} = \underbrace{\frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m}}_{\text{electron kinetic energy}} - \underbrace{\frac{e^2}{\hat{r}_{1A}} - \frac{e^2}{\hat{r}_{2A}} - \frac{e^2}{\hat{r}_{1B}} - \frac{e^2}{\hat{r}_{2B}}}_{\text{electron attraction to protons}} + \underbrace{\frac{e^2}{\hat{r}_{12}}}_{\text{electron-electron repulsion}} + \underbrace{\frac{e^2}{R}}_{\text{proton-proton repulsion}}$$

Molecular orbital model: Ignore electron-electron interaction and just "fill up" the molecular orbitals in the same way we fill atomic orbitals for a multi-electron atom. In some sense this problem is like the helium atoms, the difference being that the two electrons move in the potential created by two protons rather than an alpha particle.

Thus, two zeroth order $|\Psi^{(0)}\rangle = |1\sigma_g\rangle |1\sigma_g\rangle$

the perturbation Hamiltonian is $\hat{H}_1 = \frac{e^2}{\hat{r}_{12}}$

To zeroth order $E^{(0)} = 2E_g + \frac{e^2}{R}$

E_g found in part (b)

(nuclear repulsion counted once)

(Next Page)

The first order correction is

$$\Delta E^{(1)} = \langle \Psi^{(0)} | \frac{e^2}{r_{12}} | \Psi^{(0)} \rangle > 0$$

Note: $\Psi^{(0)}(\vec{x}_1, \vec{x}_2) = N (\underbrace{\psi_A(\vec{x}_1) + \psi_B(\vec{x}_1)}_{\psi_{0g}(\vec{x}_1)}) (\underbrace{\psi_A(\vec{x}_2) + \psi_B(\vec{x}_2)}_{\psi_{0g}(\vec{x}_2)})$

↑
normalization

$$= N \left[(\psi_A(\vec{x}_1) \psi_B(\vec{x}_2) + \psi_B(\vec{x}_1) \psi_A(\vec{x}_2)) + (\psi_A(\vec{x}_1) \psi_A(\vec{x}_2) + \psi_B(\vec{x}_1) \psi_B(\vec{x}_2)) \right]$$

The first term represents ~~both~~ electrons on different nuclei (the Heitler-London model) whereas the second term represents both electrons at the same nuclei (ionic interactions)

(d) In the Heitler-London model, we think of the molecule as forming from two neutral atoms. Thus we take as our trial wave function

$$\tilde{\Psi}(\vec{x}_1, \vec{x}_2) = c \underbrace{\psi_A(\vec{x}_1) \psi_B(\vec{x}_2)}_{\substack{\text{electron 1 at A} \\ \text{2 at B}}} + d \underbrace{\psi_B(\vec{x}_1) \psi_A(\vec{x}_2)}_{\substack{\text{electron 1 at B} \\ \text{2 at A}}}$$

Again, we expect symmetric + antisym combinations. The minimization procedure should give this result.

To facilitate the calculation, I will use Dirac notation.

$$\text{trial state: } |\tilde{\Psi}\rangle = c |\psi_A\rangle |\psi_B\rangle + d |\psi_B\rangle |\psi_A\rangle$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12}$$

$$\hat{H}_1 = \frac{\hat{p}_1^2}{2m} - \frac{e^2}{\hat{r}_{1A}} - \frac{e^2}{\hat{r}_{1B}} = \underbrace{\hat{H}_{1A}}_{\text{Hydrogen atom at A}} - \frac{e^2}{\hat{r}_{1B}} = \underbrace{\hat{H}_{1B}}_{\text{Hydrogen atom at B}} - \frac{e^2}{\hat{r}_{1A}}$$

$$\hat{H}_2 = \hat{H}_{2A} - \frac{e^2}{\hat{r}_{2B}} = \hat{H}_{2B} - \frac{e^2}{\hat{r}_{2A}}$$

$$\hat{H}_{12} = \frac{e^2}{\hat{r}_{12}}$$

Aside:

$$\hat{H}_1 |\tilde{\Psi}\rangle = c \left(\hat{H}_{1A} - \frac{e^2}{\hat{r}_{1B}} \right) |\psi_A\rangle \otimes |\psi_B\rangle + d \left(\hat{H}_{1B} - \frac{e^2}{\hat{r}_{1A}} \right) |\psi_B\rangle \otimes |\psi_A\rangle$$

$$= E_H^{(1s)} |\tilde{\Psi}\rangle + \left[c \left(-\frac{e^2}{\hat{r}_{1B}} \right) |\psi_A\rangle |\psi_B\rangle + d \left(-\frac{e^2}{\hat{r}_{1A}} \right) |\psi_B\rangle |\psi_A\rangle \right]$$

$$\Rightarrow \langle \tilde{\Psi} | \hat{H}_1 | \tilde{\Psi} \rangle = E_H^{(1s)} \langle \tilde{\Psi} | \tilde{\Psi} \rangle + (c^2 + d^2) I$$

$$+ 2cd M P_{AB}$$

$$= \langle \tilde{\Psi} | \hat{H}_2 | \tilde{\Psi} \rangle$$

where I , M , P_{AB} are defined in part (a)

The interaction term is as in Helium:

$$\langle \tilde{\Psi} | \frac{e^2}{r_{12}} | \tilde{\Psi} \rangle = (c^2 + d^2) J + 2cd K$$

where $J = \int d^3x_1, d^3x_2 \psi_A^2(\vec{x}_1) \psi_B^2(\vec{x}_2) \frac{e^2}{r_{12}}$ (Direct term)

$$K = \int d^3x_1, d^3x_2 \psi_A(\vec{x}_1) \psi_B(\vec{x}_2) \frac{e^2}{r_{12}} \psi_B(\vec{x}_1) \psi_A(\vec{x}_2)$$

(exchange term)

⇒ Variational energy

$$\bar{E}(c, d) = \frac{\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle}{\langle \tilde{\Psi} | \tilde{\Psi} \rangle} = \frac{\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle}{c^2 + d^2 + 2cd P_{AB}^2} + \frac{e^2}{R}$$

$$= 2E_H(1s) + \frac{(c^2 + d^2)(2I + J) + 2cd(2MP_{AB} + K)}{c^2 + d^2 + 2cd P_{AB}^2} + \frac{e^2}{R}$$

Minimize $\frac{\partial \bar{E}}{\partial c} = \frac{\partial \bar{E}}{\partial d} = 0 \Rightarrow c = \pm d$

⇒ Heitler-London ground states

$$E(1\Sigma_{g,u}) = 2E_H(1s) + \frac{2I + J \pm (2MP_{AB} + K)}{1 \pm P_{AB}^2} + \frac{e^2}{R}$$

where $|\tilde{\Psi}\rangle = |\psi_A\rangle|\psi_B\rangle \pm |\psi_B\rangle|\psi_A\rangle$
(unnormalized)

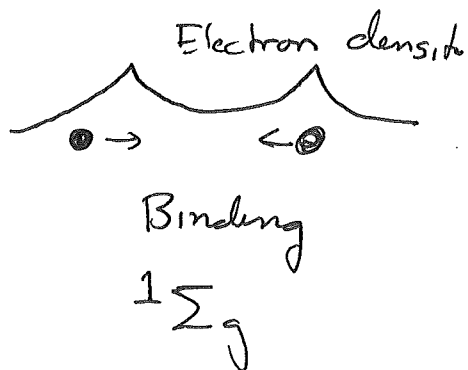
(e) The Pauli principle insists of complete antisymmetry. Thus we must have

$$|{}^1\Sigma_g\rangle = \underbrace{|\Sigma_g\rangle}_{\text{Symmetric spatial}} \otimes \underbrace{|\chi_s\rangle}_{\text{Singlet anti-sym spin}}$$

or

$$|{}^3\Sigma_u\rangle = \underbrace{|\Sigma_u\rangle}_{\text{anti symmetric spatial}} \otimes \underbrace{|\chi_T\rangle}_{\text{triplet symmetric-spin}}$$

The singlet, being symmetric spatially is binding. This makes sense physically since the symmetric state will have more of the electron charge at the origin between the nuclei, providing an attractive force. The triplet will have an anti-symmetric spatial wavefunction, providing repulsion:



A copy of the H_2 B-O potentials is shown below:

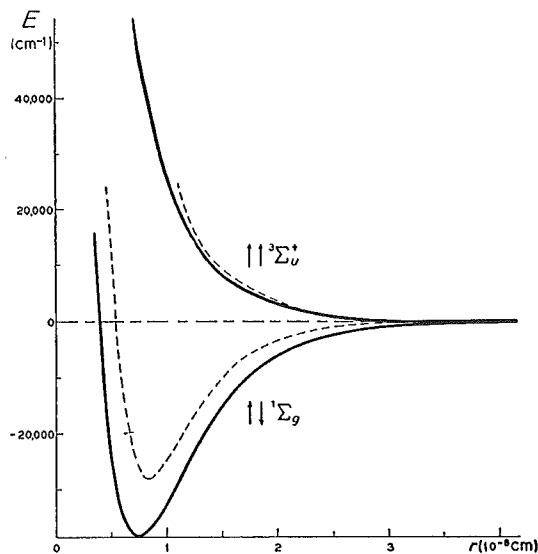


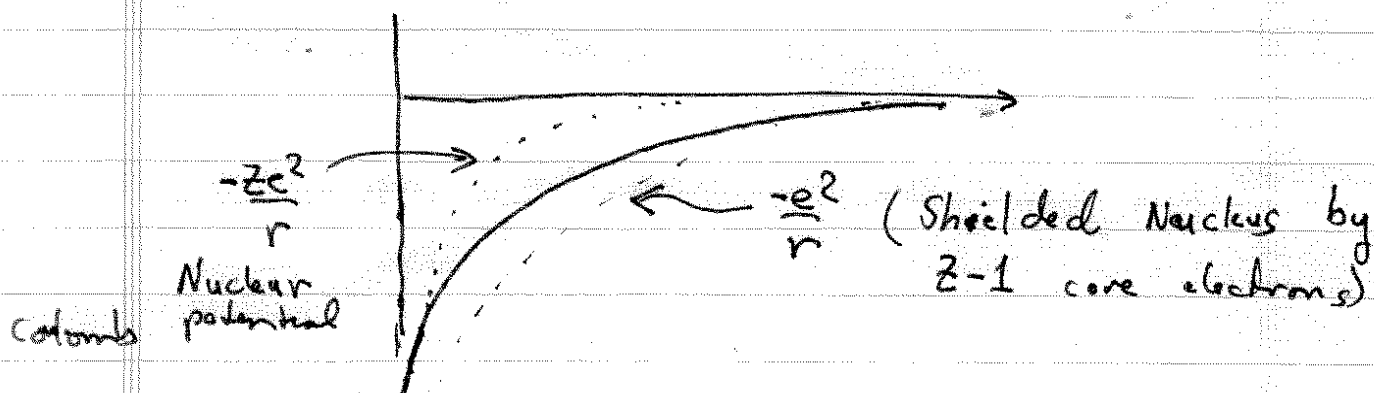
FIG. 161. Potential Curves of the Two Lowest States of the H_2 Molecule. The full line curves are the final curves resulting from the calculations of James and Coolidge (361) (859), which agree with the observed data; the broken line curves are first approximations as given by Heitler (1024a) (see p. 353 f.).

From Herzberg "Spectra of Diatomic Molecules",
Van Nostrand Reinhold, 1950

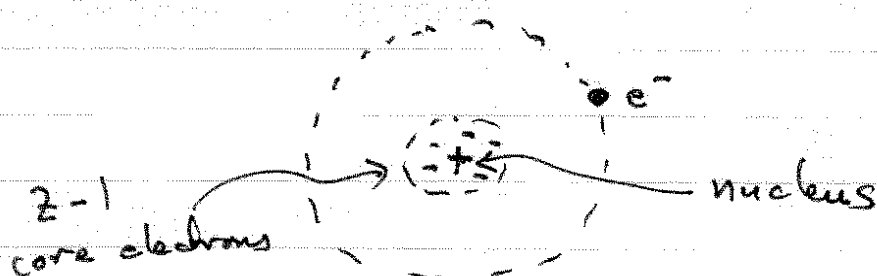
Problem 3: Spectrum of multielectron atoms

In the mean field approximation, we ignore electron correlations and then obtain a spherically symmetric charge distribution. The total potential seen by the valence electron is then the sum of the Coulomb potential due to the attraction to the nucleus plus the repulsive potential due to the other "core" electrons

$$V(r) = V_{\text{nucleus}}(r) + V_{\text{core}}(r)$$



In a Bohr like picture for an alkali with one valence electron



The question is thus, how much does the wave function associated with the valence electron penetrate the core?

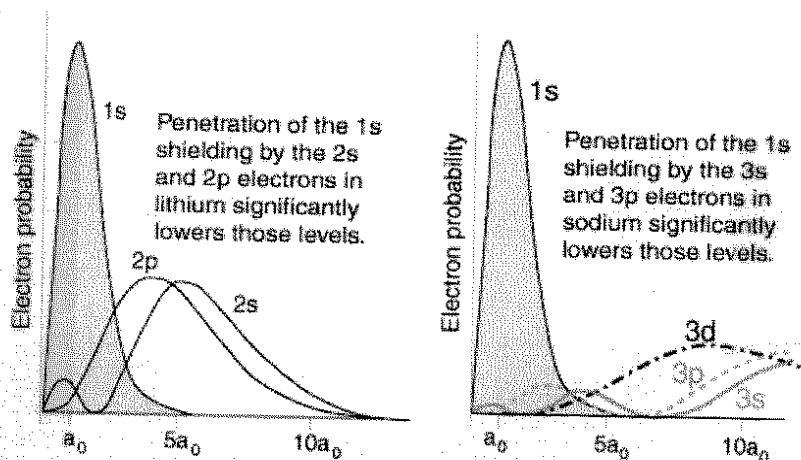
Since the potential is still spherically symmetric, the set $\{n, l, m\}$ are still "good quantum numbers". Because the radial wave functions associated with different l will have different support inside the core, the energy will be different. In particular, we expect the s -states ($l=0$) to have the lowest energy for a given n , since these are more peaked near the origin.

A nice description of this is given at the url:

<http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/orbdep.html>

Origin of Orbital Quantum Number Dependence of Electron Energies

When the wavefunctions for electrons with different orbital quantum numbers are examined, it is found that there is a different amount of penetration into the region occupied by the $1s$ electrons. This penetration of the shielding $1s$ electrons exposes them to more of the influence of the nucleus and causes them to be more tightly bound, lowering their associated energy states.



In the case of lithium, the $2s$ electron shows more penetration inside the first Bohr radius and is therefore lower than the $2p$. In the case of sodium with two filled shells, the $3s$ electron penetrates the inner shielding shells more than the $3p$ and is significantly lower in energy.

(b) Coarse but solvable model

$$V(r) = -\frac{e^2}{r} + \frac{A}{r^2}$$

Radial eq.

$$-\frac{1}{2} \frac{d^2 u}{d\bar{r}^2} + \left(\frac{l(l+1) + \bar{A}}{2\bar{r}^2} - \frac{1}{\bar{r}} \right) u = -\epsilon u$$

where $\bar{r} = \frac{r}{a_0}$ $\epsilon = -E / \frac{e^2}{a_0}$ binding energy
Bohr radius

$$\bar{A} = \frac{2A}{\hbar^2}$$

This is the same form of the radial equation as for Hydrogen, except $l(l+1) \rightarrow l(l+1) + \bar{A}$

Thus let $s(s+1) = l(l+1) + \bar{A}$

Making the Ansatz (as we did for Hydrogen)

$$u(\bar{r}) = \bar{r}^{s+1} e^{-K\bar{r}} F(\bar{r}) \quad K = \sqrt{2\epsilon}$$

We arrive at the Laguerre eq. with eigenfunction $L_{n_r}^{2s+1}(K\bar{r})$

Eigenvalue $K = \frac{1}{n_r + s + 1} = \sqrt{2\epsilon}$

$$\Rightarrow \epsilon = \frac{1}{2(n_r + s + 1)^2} \quad (\text{Next Page})$$

$$\rightarrow E = \frac{-R}{2(n_r + s + 1)^2} \quad R = \frac{e^2}{2a_0} = 13.6 \text{ eV}$$

Now we must solve for s in terms of l and A :

$$s^2 + s - (l(l+1) + \bar{A}) = 0$$

$$\Rightarrow s = -\frac{1}{2} + \frac{1}{2} \sqrt{1 + (4l(l+1) + \frac{8mA^2}{\hbar^2})}$$

↑
must choose (+)-sign to make $s > 0$

$$\Rightarrow s+1 = \frac{1}{2} \left(1 + \sqrt{(2l+1)^2 + \frac{8mA^2}{\hbar^2}} \right)$$

$$\therefore E_{n_r, l} = \frac{-R}{\left[n_r + \frac{1}{2} \left(1 + \sqrt{(2l+1)^2 + \frac{8mA^2}{\hbar^2}} \right) \right]^2}$$

Check $A \rightarrow 0$ $E_{n_r, l} = \frac{-R}{(n_r + l + 1)^2}$ as expected

Performing a power series expansion

$$E_{n_r, l} = \frac{-R}{(n_r + l + 1)^2} + \frac{R(2A)}{(n_r + l + 1)^3 (2l + 1)}$$

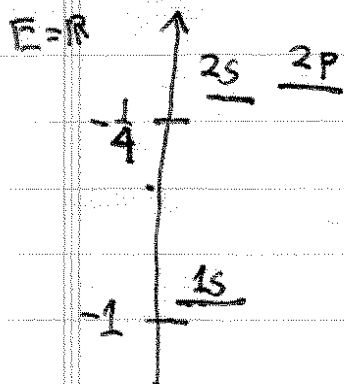
⏟
Perturbation #

(Next Page)

⊙ In terms of principle q-number:

$$E_{n,l} = -\frac{R}{n^2} \left(1 - \frac{\bar{A}}{(l+\frac{1}{2})n} \right)$$

Sketch:



← degeneracy broken

$2s$ is lower energy than $2p$

Note $\frac{R\bar{A}}{n^3(l+\frac{1}{2})}$

follows from first order perturbation theory

$$E^{(1)} = \langle n,l | \frac{A}{r^2} | n,l \rangle = \frac{\hbar^2 \bar{A}}{2ma_0^2} \langle n,l | \frac{1}{r^2} | n,l \rangle$$

$$= R\bar{A} \frac{1}{n^3(l+\frac{1}{2})} \quad \text{as expected.}$$