

IDEAL FERMIONS SOL

(a) All doublets, $E_0 = -10$, $\omega = 6, 8, 9$, IP = 10

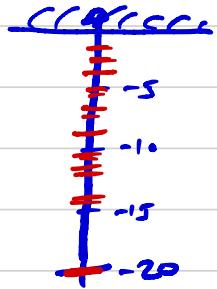


(b) $E_0 = -20$; $-14, -12, -11, -8, -6, -5, -4, -3, -2$

1 2 2 2 1 2 2 1 2 1

$i = s$ (9)

$z = s, t$ (4)



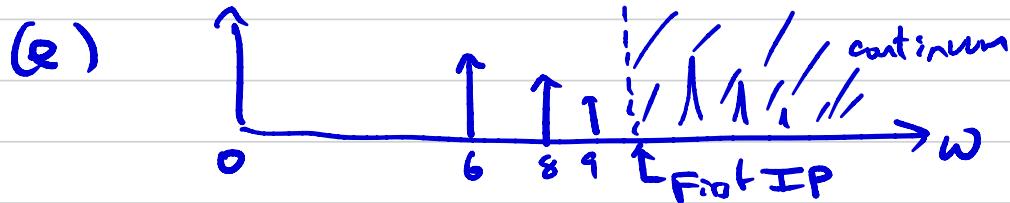
(c)

-	$\overline{\overline{+}}$	$\overline{+}$	$\overline{+}$	$\overline{\overline{+}}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$
$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$
-20	-14	-12	-11	-8	-6	-5	-4	-3	-2
gs	singles				doublet				

$$\Psi_{\text{g}}(1,2) = \Phi_0(x_1)\Phi_0(x_2)X_{\text{singl}} \quad \text{gs}$$

$$\begin{aligned} \Psi_{\text{g}}(1,2) &= \frac{1}{2} (\Phi_0(x_1)\Phi_0(x_2) + \Phi_0(x_1)\Phi_0(x_2)) X_{\text{singl}} \xrightarrow{\text{11s}} \\ &= \frac{1}{2} (\Phi_0(x_1)\Phi_0(x_2) - \Phi_0(x_1)\Phi_0(x_2)) X_{\text{trip}} \xleftarrow[\text{1s}]{\text{11s} + \text{17s}} \end{aligned}$$

(d) All triplets shift down, singles up a little.



(f)

$\overline{\overline{+}}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$
$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$	$\overline{+}$
-20	-14	-11	-8	-6	-5	-4	-3	-2
-28	-26	-25	-24	-23	-22	-20	-19	-18
gs	single excitation			double excitation		core excitations		

IP is at -24, so most doublets + core not bound.

HE WITH EXPONENTIALS

a) $\hat{H} = -\frac{1}{2}(V_1^2 + V_2^2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{(r_1 - r_2)}$

b) $\Psi_0^{\text{HF}} = \Phi_0(r_1) \Phi_0(r_2) \chi_{\text{sym}}(\sigma \Sigma)$

c) $T[\phi] = \frac{1}{2}, V[\phi] = -2$; here $\gamma = 2 \Rightarrow t = 2, r = -t, \epsilon = -2$

Then $E = 2\epsilon + U_{\frac{1}{2}} = -4 + \frac{5}{4} = -2.75 = -74.8 \text{ eV}$ (4% error)

For He^+ , $E = -2 \Rightarrow I = 0.75 = 20.4 \text{ eV}$ vs HF 25.6 eV (20% err)

d) $t = \frac{r^2}{2}, r = -2\gamma, U = \frac{5\gamma}{8} \Rightarrow E = \gamma^2 - 2\left(2 - \frac{5}{16}\right)\gamma$

$$\Rightarrow \gamma_m = Z_{\text{eff}} = 2 - \frac{5}{16} = 1.6875 \Rightarrow E = -\gamma_m^2 = -2.848 = -77.5 \text{ eV}$$

$\Rightarrow \text{IP} \approx 23.1 \text{ eV}$ or 6% underestimate

e) In (c) $T = 4, V = -8 + \frac{5}{4} \Rightarrow -\frac{V}{2T} = 1 - \frac{5}{32}$ instead of 1 (5% err)

In (d) $T(\gamma_m) = -\frac{1}{2}V(\gamma_m) \Rightarrow -\frac{V}{2T} = 1$ exactly satisfied.

f) $Z_{\text{eff}} < 2$, because bare Coulomb attraction to nucleus is partially screened by 'other' electron

g) For Li^+ , $E^{\text{HF}} = -\gamma_m^2, \gamma_m = 3 - \frac{5}{16}; E = -7.222; E(\text{Li}^{++}) = -4.5$

$$\Rightarrow \text{IP}^{\text{HF}} = 2.722, \text{ exact HF is } -7.236 \Rightarrow \text{IP}^{\text{HF}} = 2.736 \Rightarrow \text{err} < 1\%$$

\Rightarrow orbital much closer to hydrogenic as repulsion weaker (rel).

SOL TO ITERATION

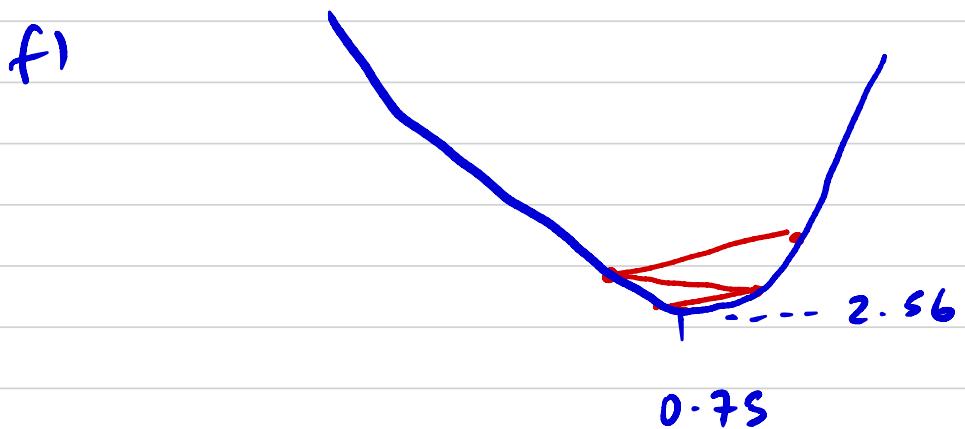
a) $f' = x^5 + x - 1 = 0 \Rightarrow x = (1-x)^{1/5}$ at min.

b)	start at 0.5	k	$x_n^{(k)}$	$f(x_n^{(k)})$
		1	0.870	2.581
		2	0.664	2.571
		3	0.804	2.564
		:		
		10	0.753	2.560886
		:		
		20	0.75496	2.56088204

c) Use k=20 as answer & figure out errors

d) start at 0.75, get there much quicker

e) Gets stuck oscillating between 0 and 1. Fix by mixing some fraction of old guess with new guess, but converges slower



SPECTRUM N ATOM SOL

GS: N: [Be] $2p^3$; look up list (table 11.2): 4S , 2D , 2P

(a) 14.48 eV ($\sim \frac{1}{2}\text{H}$, $\sim 340\text{ kcal}$, $\sim 17,000\text{ cm}^{-1}$); gap = 2.2 eV

(b) $2s^2 2p^6(2s)$; $2s^2 2p^2 np(5s)$; $2s^2 2p^2 ns(1s)$; $2s^2 2s nd(9s)$; $2s 2p^4(12)$...
 $(n=3,4)$ $(n=3-7)$ $(n=3+7)$

(c) Violations: np ($n \geq 2$) where 2S below 2D
 nd ($n > 3$) . . . 2P below 4F .
- both have two open shells!

(d) Valence: $2p$ (no charge in n)

Core: None, as all in continuum
(semicore $2s 2p^6$).

No doublets: (all in continuum); lowest would be maybe
 $2s^2 2p 3s^2$.

ADDITION OF ANG MOM SOL

(a) $\ell_1 = 1, \ell_2 = 1 \Rightarrow L = 2, 1, 0 \Rightarrow S+3+1=9$
 $(3 \times 3)=9$

(b) $|m_1=1, m_2=1\rangle = |L=2, M_L=2\rangle$

(c) $L_- |L=2, M=2\rangle = \sqrt{2(3-2)} |2, 1\rangle = 2 |2, 1\rangle$

$$(L_{1,-} + L_{2,-}) |M_1=1, M_2=1\rangle = \sqrt{2(1-1)} (|0, 1\rangle + |1, 0\rangle)$$

$$\Rightarrow |2, 1\rangle = \frac{1}{\sqrt{2}} (|0, 1\rangle + |1, 0\rangle)$$

(d) $\ell=1, s=\frac{1}{2} \Rightarrow 3 \times 2 = 6$ states; two of these $\Rightarrow 6 \times 6 = 36$
 $L = 2, 1, 0, S = 1, 0 \Rightarrow ^3D, ^1D, ^3P, ^1P, ^3S, ^1S$.
of states is $(S+3+1) \times (3+1) = 36$

With Pauli exclusion, only $^3D, ^3P, ^1S$ allowed (15)

(e) For $^3D, L=2, S=0 \Rightarrow J=2 \Rightarrow ^3S; ^1S, L=S=0 \Rightarrow J=0, \Rightarrow 1; ^3P: J=2, 1, 0 \Rightarrow S+3+1=9$

(f) $|J=2, M_J=2\rangle = |L=1, S=1\rangle$

$$J_- |2, 2\rangle = 2 |2, 1\rangle$$

$$(L_{-} + S_{-}) |2, 1\rangle = \sqrt{2} (|0, 1\rangle + |1, 0\rangle) + \text{same as before.}$$

KOOPMANS' SOL

(a) $E^{HF} = -2.861$, $E = -2.903$

$$\% \text{ Error} = 100 \left(\frac{\text{approx} - \text{exact}}{\text{exact}} \right) = -\frac{4}{290} \approx -1.3\%, \text{ yes } E^{HF} > E$$

(b) For He^+ , $E^{HF} = -2$, exact answer.

(c) $I^{HF} = 0.861$, $I = 0.903 \Rightarrow \% \text{ error} = -5\% = -10\text{eV}$, VP $\Rightarrow I^{HF} < I$.

(d) $-E^{HF} = 0.918 \approx I^{HF}$ (only approx); $\% \text{ error} = +1.5\%$; better estimate.

(e) Errors get smaller (see last part of He with exponential problem).

BASIS SET SOLS

(a) $\text{STO-3G} < \text{3-21G} < \text{6-311G}^{**}$ for He^+

(b) Same for He, so consistent.

(c) For He^+ , $E = -2$
For He, $E^{\text{HF}} = -2.861$ ΔE

	STO-3G	3-21G	6-311G ^{**}
0.068	0.025	0.002	
0.053	0.025	0.001	

(d)

$$\text{IP} = E(\text{He}^+) - E(\text{He})$$

	STO-3G	3-21G	6-311G ^{**}
0.876	0.861	0.862	

(e) ΔIP

$$0.015 \quad - \quad 0.001$$

Errors in IP much smaller than errors in total energies, due to cancellation.

(f) No, VP does not help, as no way to know which calc has the larger basis-set error.

Chem231B: Assignment #3

February 9, 2020

Problems from Berry, Rice, and Ross

a) Do problems 10, 12, 14, 15, and 18 from BRR. For reference data, use the NIST website, Atomic Spectra Database. (This replaced Moore's tables, and the NBST became NIST). Also check out the Computational Chemistry Comparison and Benchmark DataBase (cccbdb) from which I got some of the basis-set results.

10) Put entries in the following sets of configurations in order of increasing energy. Then check your intuition with experimental results at NIST Spectra Database.

a) Li, $1s^2 2s, 1s^2 2p, 1s2s2p, 1s2s^2$

b) C, $1s^2 2s^2 2p^2, 1s^2 2s2p^3, 1s^2 2s^2 2p3s, 1s2s^2 2p^3$

12) Explain why the second ionization potential of lithium for the process $\text{Li}^+ \rightarrow \text{Li}^{2+} + e^-$, is less than that predicted for a hydrogenlike atom with $Z = 3$.

The electronic repulsion from the two electrons within lithium ion leads to smaller second ionization potential than predicted by a hydrogenlike atom which only has one electron.

14) The outer electron of an alkali atom may be treated in an approximate way, as if it were in a hydrogenic orbital. Suppose that one takes the quantum number for the outer electron to be 2, 3, 4, 5, and 6, respectively, for Li, Na, K, Rb, and Cs. What values must Z be given to account for the observed first ionization potentials of these atoms? Explain why they differ from unity.

Look up first ionization potential (IP) energy on NIST and solve for Z within the Rydberg equation where the HOMO may be taken as the IP energy from Koopman's Theorem.

For lithium atom, the ionization potential energy is 5.3917eV

$$\frac{13.6Z^2}{2^2} = 5.3917$$

$$Z^2 = \frac{4 * 5.3917}{13.6}$$

$$Z = \{\pm 1.259\}$$

Z value for lithium is 1.259. Repeat for Na, K, Rb, and Cs

Atom	<i>Z</i>
Li	1.259
Na	1.229
K	1.130
Rb	1.108
Cs	1.070

When *Z* = 1, this indicates an unscreened electron from the hydrogen atom. The *Z* values are differ from unity because the nuclear attraction is increasing while at the same time, the screening effect does not exactly cancel with the attraction.

15) Use the Pauli exclusion principle and Hund's rules to find the number of unpaired electrons and the term of lowest energy for the following atoms.

a) P: [Ne]3s²3p³; *L* = 0 and *S* = $\frac{3}{2}$ and *J* = *L* + *S* = $\frac{3}{2}$; Term Symbol: ${}^4S_{\frac{3}{2}}$

b) S: [Ne]3s²3p⁴; *L* = 1 and *S* = 1 and *J* = 2; Term Symbol: 3P_2

c) Ca: [Ar]4s²; *L* = 0 and *S* = 0 and *J* = 0; Term Symbol: 1S_0

d) Br: [Ar]4s²3d¹⁰4p⁵; *L* = 1 and *S* = $\frac{1}{2}$ and *J* = $\frac{3}{2}$; Term Symbol: ${}^2P_{\frac{3}{2}}$

e) Fe: [Ar]4s²3d⁶; *L* = 2 and *S* = 2 and *J* = 4; Term Symbol: 5D_4

18) Derive the terms of the configuration 1s²2s²2p⁶3s²3p3d, of the silicon atom.

S = 1 and *L* = 3 and *J* = {2, 3, 4}; Term Symbols: ${}^3F_2, {}^3F_3, {}^3F_4$

Sols to ELEMENT 168

2. Real periodic table :

row	1	2	3	4	5	6	7
Z _{noble}	2	10	18	36	54	84	118
Z _{n/2}	1	5	9	18	9	27	43
difference	4	4	9	9	16	16	59

$$\lfloor \frac{n}{2} + 1 \rfloor \quad 1 \quad 2 \quad 2 \quad 3 \quad 3 \quad \text{Lxj = integer part of } x$$

Try $Z_{nn} = Z_n + 2 \lfloor \frac{n}{2} + 1 \rfloor^2$
 $Z_1 = 2^1^2 = 2, Z_2 = 2 + 2 \cdot 4 = 10, Z_3 = 10 + 2 \cdot 4 = 18 \checkmark$

widths:	row	1	2	3	4	5	...
width		2	8	8	18	18	

$$\text{widths: } W_n = 2 \lfloor \frac{n}{2} + 1 \rfloor^2, Z_{nn} = Z_n + W_{n+1}$$

$$W_8 = 50, W_9 = 50, W_{10} = 72 = W_{11}$$

$$\Rightarrow Z_8 = 168, Z_9 = 218, Z_{10} = 290$$

So for 217, config is noble gas with a p hole, $^2P_{3/2}$.

Non interacting:

	s	p	d	f	g	h	i
$Z_{nn} = Z_n + 2n^2$; n	1	2	3	4	5	6	7
Z_n	2	10	28	60	110	182	280

So open shell has $217 - 182 = 35$ occupied orbitals. All degenerate. Possibly including i orbitals.