Lecture Thursday 13. September 2007

Topics: Many.elecron atoms part 1 (with additional material – Ionization potentials etc)

The interaction between charges -> interaction of e- with a charge-cloud

$$W(\vec{r}) = \int \frac{(-e)^2 \sum_{i=1}^{N} |\psi_i(\vec{x})|^2}{|\vec{r} - \vec{x}|} \, d^3x$$

The total energy - or potential which "every electron feels"

$$T_{r_1} - \frac{Ze^2}{r_1} + \int d^3x \, \frac{P_1(\vec{x})}{|\vec{r} - \vec{x}|} \qquad P_1 = \sum |\psi_i|^2$$

$$\left\{ T_{r_1} - \frac{Ze^2}{r_1} + \int d^3x \, \frac{P_1(\vec{x})}{|\vec{r} - \vec{x}|} \right\} \varphi_1(\vec{r}_1) = E \varphi_1(\vec{r}_1)$$

built from the "assumed" states of other electrons

charge-cloud – probability density

$\varphi_1^{(0)}(\vec{r})\ \varphi_2^{(0)}(\vec{r})\ \ldots\ldots\ \varphi_N^{(0)}(\vec{r})$ assumed wavefunctions

$$p^{(1)}(\vec{r}) = \sum_{i=1}^{N} \left|\varphi_i^{(0)}\right|^2$$

N-equations for $i = 1 \ldots N$

$$\left\{ T_{r_1} - \frac{Ze^2}{r_1} + e^2 \int d^3x \frac{p^{(1)}(\vec{x})}{|\vec{r} - \vec{x}|} \right\} \varphi_i^{(1)}(\vec{r}_1) = E\, \varphi_i^{(1)}(\vec{r}_1)$$

Solve numerically

$\varphi_1^{(1)}(r)\ \varphi_2^{(1)}(r)\ \ldots\ \ldots\ \varphi_N^{(1)}(\vec{r})$ Obtained

$$p^{(2)}(\vec{r}) = \sum_{i=1}^{N} \left|\varphi_i^{(1)}\right|^2$$

$$\left\{ T_{r_1} - \frac{Ze^2}{r_1} + e^2 \int d^3x \frac{p^{(2)}(\vec{x})}{|\vec{r} - \vec{x}|} \right\} \varphi_i^{(2)}(\vec{r}_1) = E\, \varphi_i^{(2)}(\vec{r}_1)$$

Iteration – i.e. repeated trials

$$\left\{ T_{r_1} - \frac{Ze^2}{r_1} + e^2 \int d^3x \, \frac{P^{(m)}(\vec{x})}{|\vec{r} - \vec{x}|} \right\} \varphi_i^{(m)}(\vec{r}_1) = E \, \varphi_i^{(m)}(\vec{r}_1)$$

$$\varphi_i^{(0)} \longrightarrow P^{(1)} \longrightarrow W^{(1)} \xrightarrow{\text{Schrödinger}} \varphi_i^{(1)}$$

$$\varphi_1^{(1)} \longrightarrow P^{(2)} \longrightarrow W^{(2)} \longrightarrow \varphi_1^{(2)}$$

$$\varphi_1^{(2)} \longrightarrow P^{(3)} \longrightarrow W^{(3)} \longrightarrow \varphi_1^{(3)}$$

$$\varphi_i^{(m)} \longrightarrow P^{(m+1)} \longrightarrow W^{(m+1)} \longrightarrow \varphi_i^{(m+1)}$$

When to stop ?? ⟶ Self-consistency

$$\int \left(P^{(m)} - P^{(m+1)} \right) d^3x \leq \varepsilon \quad (\varepsilon = 10^{-12} \ldots ??)$$

HARTREE – 1930's Hartree's method

What we should know:

2s 2p have the same energy in H and H-like

3s 3p 3d have the same energy in H and H-like

4s 4p 4d 4f have the same energy in H and H-like

in screened potential

2s comes under 2p

3s comes under 3p which is under 3d

for Argon and transition to Sodium

4s comes deep under 3d etc etc

Exercise on Qualitative SCF

The n,l states sequence in SCF potential

is influenced by the centrifugal barrier

See the table of ionization potentials below

The qualitative Hartree method allows us to describe the periodic table (or understand it)

2, 10, 28, ... $\sum 2n^2$ ....

2, 10, 18, ...

But for "applications" — too weak

1. deficiency → MISSING EXCHANGE

Exercise: try to formulate He as Hartree problem → and compare it with the exchange terms inclusion

$E_a + E_b + I_{ab} - K_{ab}$ triplets

$E_a + E_b + I_{ab} + K_{ab}$ singlets

Slater determinant story

Ionization Potentials

Z	Sym	Name	[eV]	core	Configuration
1	H	Hydrogen	13,60		(1s)
2	He	Helium	24,59		(1s)2
3	Li	Lithium	5,39	[He]	(2s)
4	Be	Beryllium	9,32	[He]	(2s)2
5	B	Boron	8,30	[He]	(2s)2 (2p)
6	C	Carbon	11,26	[He]	(2s)2 (2p)2
7	N	Nitrogen	14,53	[He]	(2s)2 (2p)3
8	O	Oxygen	13,62	[He]	(2s)2 (2p)4
9	F	Fluorine	17,42	[He]	(2s)2 (2p)5
10	Ne	Neon	21,56	[He]	(2s)2 (2p)6
11	Na	Sodium	5,14	[Ne]	(3s)
12	Mg	Magnesium	7,65	[Ne]	(3s)2
13	Al	Aluminum	5,99	[Ne]	(3s)2 (3p)
14	Si	Silicon	8,15	[Ne]	(3s)2 (3p)2
15	P	Phosphorus	10,49	[Ne]	(3s)2 (3p)3
16	S	Sulfur	10,36	[Ne]	(3s)2 (3p)4
17	Cl	Chlorine	12,97	[Ne]	(3s)2 (3p)5
18	Ar	Argon	15,76	[Ne]	(3s)2 (3p)6

2 particles – simple – determinant – generalize for many

2 functions $\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)$

$$\begin{vmatrix} \varphi_a(1) & \varphi_a(2) \\ \varphi_b(1) & \varphi_b(2) \end{vmatrix} \longrightarrow$$

n electrons

$$\begin{vmatrix} \varphi_a(1) & \varphi_a(2) & \cdots & \cdots \\ \varphi_b(1) & \varphi_b(2) & \cdots & \\ \varphi_c(1) & \vdots & & \\ \vdots & & & \\ \varphi_z(1) & \cdots & \cdots & \end{vmatrix}$$

Slater determinant

This will be antisymmetric due to the properties of determinants

For Lithium ... Z=3

$\psi_{abc}(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ ← Slaterdeterm
[still independent particles but antisymmetrized]

$$T_1 + T_2 + T_3 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} - \frac{Ze^2}{r_3} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} + \frac{e^2}{|\vec{r}_2 - \vec{r}_3|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_3|}$$

n	n!
2	2
3	6
4	24

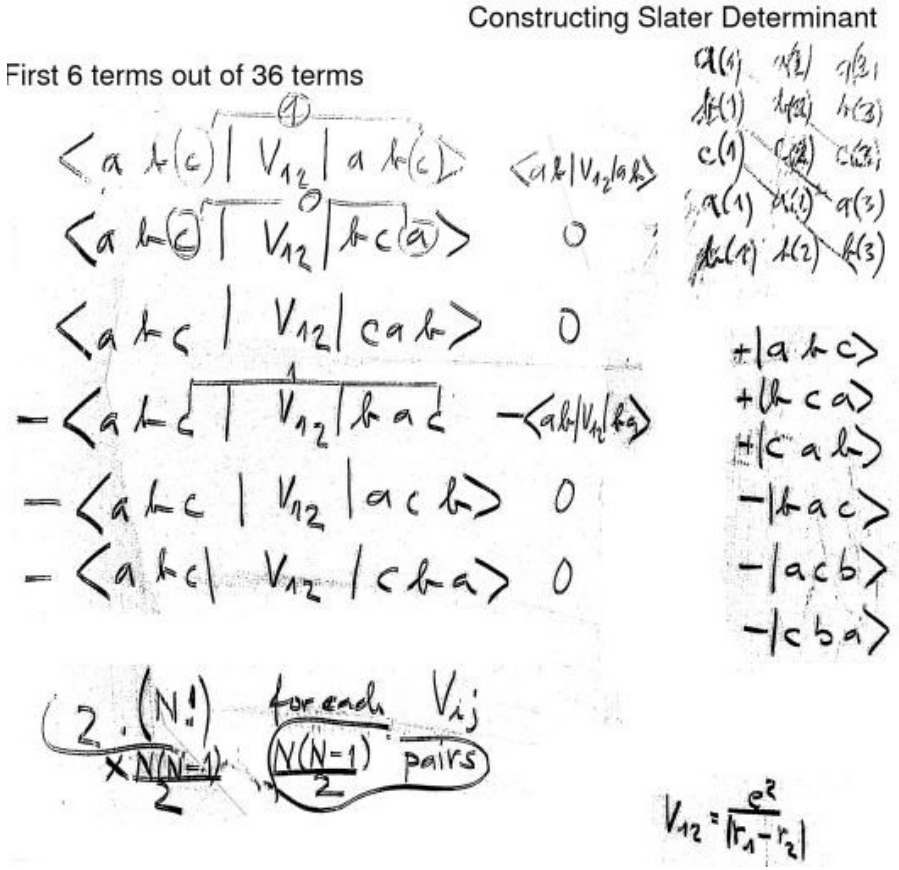
Again, take normalization 3x3 determinant has 6 terms ... n!

$(n!)\cdot(n!)$ terms
⟶ but only $(n!)$ are nonzero [each with itself only]

$$\psi_{abc}(r_1 r_2 r_3) = \sqrt{\frac{1}{3!}}\ \text{Slater}\begin{pmatrix} a & b & c \\ r_1 & r_2 & r_3 \end{pmatrix}$$

single particle operators give all just ONE from n!

From 2006 work



The collection of all the terms (2006 work)

3 particles r_1 r_2 r_3 in three orbitals $|a\rangle|b\rangle|c\rangle$

$$\langle a|T_1+V_1|a\rangle + \langle b|T_1+V_1|b\rangle + \langle c|T_1+V_1|c\rangle$$

Hartree only direct terms

$$\langle ab|V_{12}|ab\rangle + \langle ac|V_{12}|ac\rangle + \langle bc|V_{12}|bc\rangle$$

$$-\langle ab|V_{12}|ba\rangle - \langle ac|V_{12}|ca\rangle - \langle bc|V_{12}|cb\rangle$$

Hartree - neglects

Hartree - Fock

Hartree Fock also exchange terms

Sum over pairs of coordinates --> Sum over pairs of orbitals (wavefunctions)

$$+\frac{e^2}{|\vec{r}_1-\vec{r}_2|} + \frac{e^2}{|\vec{r}_2-\vec{r}_3|} + \frac{e^2}{|\vec{r}_1-\vec{r}_3|}$$

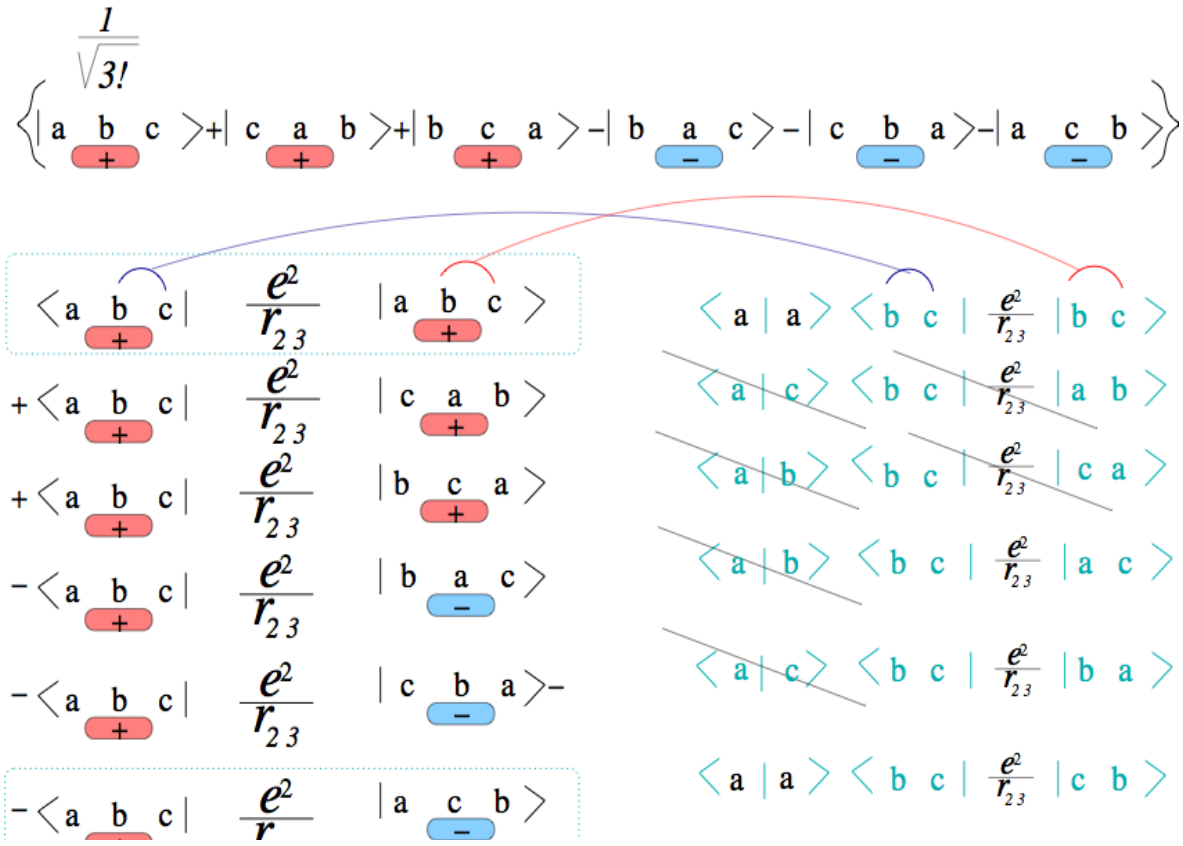
Sum over pairs of coordinates

→ Sum over pairs of "orbitals" (states, $\varphi_a, \varphi_b \ldots$)

Direct terms and exchange terms

$$E_a + E_b + E_c + I_{ab} - K_{ab} + I_{ac} - K_{ac} + I_{bc} - K_{bc}$$

2007 replacement of the 2006 work -- First 6 terms out of 36 terms



Ionization Potentials

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16	S	Sulfur	10,36	[Ne]	(3s)2 (3p)4
17	Cl	Chlorine	12,97	[Ne]	(3s)2 (3p)5
18	Ar	Argon	15,76	[Ne]	(3s)2 (3p)6

19	K	Potassium	4,34	[Ar]	(4s)
20	Ca	Calcium	6,11	[Ar]	(4s)2
21	Sc	Scandium	6,54	[Ar]	(3d) (4s)2
22	Ti	Titanium	6,82	[Ar]	(3d)2 (4s)2
23	V	Vanadium	6,74	[Ar]	(3d)3 (4s)2
24	Cr	Chromium	6,77	[Ar]	(3d)5 (4s)
25	Mn	Manganese	7,44	[Ar]	(3d)5 (4s)2
26	Fe	Iron	7,87	[Ar]	(3d)6 (4s)2
27	Co	Cobalt	7,86	[Ar]	(3d)7 (4s)2
28	Ni	Nickel	7,64	[Ar]	(3d)8 (4s)2
29	Cu	Copper	7,73	[Ar]	(3d)10 (4s)
30	Zn	Zinc	9,39	[Ar]	(3d)10 (4s)2
31	Ga	Gallium	6,00	[Ar]	(3d)10 (4s)2 (4p)
32	Ge	Germanium	7,90	[Ar]	(3d)10 (4s)2 (4p)2
33	As	Arsenic	9,81	[Ar]	(3d)10 (4s)2 (4p)3
34	Se	Selenium	9,75	[Ar]	(3d)10 (4s)2 (4p)4
35	Br	Bromine	11,81	[Ar]	(3d)10 (4s)2 (4p)5
36	Kr	Krypton	14,00	[Ar]	(3d)10 (4s)2 (4p)6
37	Rb	Rubidium	4,18	[Kr]	(5s)
38	Sr	Strontium	5,70	[Kr]	(5s)2

39	Y	Yttrium	6,38	[Kr]	(4d)	(5s)2	
40	Zr	Zirconium	6,84	[Kr]	(4d)2	(5s)2	
41	Nb	Niobium	6,88	[Kr]	(4d)4	(5s)	
42	Mo	Molybden	7,10	[Kr]	(4d)5	(5s)	
43	Tc	Technetium	7,28	[Kr]	(4d)5	(5s)2	
44	Ru	Ruthenium	7,37	[Kr]	(4d)7	(5s)	
45	Rh	Rhodium	7,46	[Kr]	(4d)8	(5s)	
46	Pd	Palladium	8,34	[Kr]	(4d)10		
47	Ag	Silver	7,58	[Kr]	(4d)10	(5s)	
48	Cd	Cadmium	8,99	[Kr]	(4d)10	(5s)2	
49	In	Indium	5,79	[Kr]	(4d)10	(5s)2	(5p)
50	Sn	Tin	7,34	[Kr]	(4d)10	(5s)2	(5p)2
51	Sb	Antimony	8,64	[Kr]	(4d)10	(5s)2	(5p)3
52	Te	Tellurium	9,01	[Kr]	(4d)10	(5s)2	(5p)4
53	I	Iodine	10,45	[Kr]	(4d)10	(5s)2	(5p)5
54	Xe	Xenon	12,13	[Kr]	(4d)10	(5s)2	(5p)6
55	Cs	Cesium	3,89	[Xe]	(6s)		
56	Ba	Barium	5,21	[Xe]	(6s)2		
57	La	Lanthanum	5,58	[Xe]	(5d)	(6s)2	
58	Ce	Cerium	5,54	[Xe]	(4f)	(5d)	(6s)2

59	Pr	Praseodym.	5,46	[Xe] (4f)3 (6s)2
60	Nd	Neodymium	5,53	[Xe] (4f)4 (6s)2
61	Pm	Promethium	5,55	[Xe] (4f)5 (6s)2
62	Sm	Samarium	5,64	[Xe] (4f)6 (6s)2
63	Eu	Europium	5,67	[Xe] (4f)7 (6s)2
64	Gd	Gadolinium	6,15	[Xe] (4f)7 (5d) (6s)2
65	Tb	Terbium	5,86	[Xe] (4f)9 (6s)2
66	Dy	Dysprosium	5,94	[Xe] (4f)10 (6s)2
67	Ho	Holmium	6,02	[Xe] (4f)11 (6s)2
68	Er	Erbium	6,10	[Xe] (4f)12 (6s)2
69	Tm	Thulium	6,18	[Xe] (4f)13 (6s)2
70	Yb	Ytterbium	6,25	[Xe] (4f)14 (6s)2
71	Lu	Lutetium	5,43	[Xe] (4f)14 (5d) (6s)2
72	Hf	Hafnium	6,65	[Xe] (4f)14 (5d)2 (6s)2
73	Ta	Tantalum	7,89	[Xe] (4f)14 (5d)3 (6s)2
74	W	Tungsten	7,98	[Xe] (4f)14 (5d)4 (6s)2
75	Re	Rhenium	7,88	[Xe] (5f)14 (5d)5 (6s)2
76	Os	Osmium	8,70	[Xe] (4f)14 (5d)6 (6s)2
77	Ir	Iridium	9,10	[Xe] (4f)14 (5d)7 (6s)2
78	Pt	Platinum	9,00	[Xe] (4f)14 (5d)9 (6s)

79	Au	Gold	9,23	[Xe]	(4f)14 (5d)10 (6s)
80	Hg	Mercury	10,44	[Xe]	(4f)14 (5d)10 (6s)2
81	Tl	Thallium	6,11	[Xe]	(4f)14 (5d)10 (6s)2 (6p)
82	Pb	Lead	7,42	[Xe]	(4f)14 (5d)10 (6s)2 (6p)2
83	Bi	Bismuth	7,29	[Xe]	(4f)14 (5d)10 (6s)2 (6p)3
84	Po	Polonium	8,42	[Xe]	(4f)14 (5d)10 (6s)2 (6p)4
85	At	Astatine	9,65	[Xe]	(4f)14 (5d)10 (6s)2 (6p)5
86	Rn	Radon	10,75	[Xe]	(4f)14 (5d)10 (6s)2 (6p)6
87	Fr	Francium	3,83	[Rn]	(7s)
88	Ra	Radium	5,28	[Rn]	(7s)2
89	Ac	Actinium	5,17	[Rn]	(6d) (7s)2
90	Th	Thorium	6,08	[Rn]	(6d)2 (7s)2
91	Pa	Protactini.	5,89	[Rn]	(5f)2 (6d) (7s)2
92	U	Uranium	6,05	[Rn]	(5f)3 (6d) (7s)2
93	Np	Neptunium	6,19	[Rn]	(5f)4 (6d) (7s)2
94	Pu	Plutonium	6,06	[Rn]	(5f)6 (7s)2
95	Am	Americium	5,99	[Rn]	(5f)7 (7s)2
96	Cm	Curium	6,02	[Rn]	(5f)7 (6d) (7s)2
97	Bk	Berkelium	6,23	[Rn]	(5f)8 (6d) (7s)2
98	Cf	Californium	6,30	[Rn]	(5f)10 (7s)2

99	Es	Einsteinium	6,42		[Rn]	(5f)11	(7s)2
100	Fm	Fermium	6,50		[Rn]	(5f)12	(7s)2
101	Md	Mendelev.	6,58		[Rn]	(5f)13	(7s)2
102	No	Nobelium	6,65		[Rn]	(5f)14	(7s)2
103	Lr	Lawrencium	4,87		[Rn]	(5f)14 (6d)	(7s)2
104	Rf	Rutherfordium		6,01			