Appendix B: Concepts on Hartree and Hartree-Fock Approximations

- An introduction to the complexity of IPA[+]
- Helium atom (in atomic units)

$$\hat{H} = \left(-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1}\right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{2}{r_2}\right) + \frac{1}{r_{12}} \qquad (B1) \qquad r_{12} \equiv |\vec{r}_1 - \vec{r}_2|$$

  - hope to retain concept of single-electron states (OR "atomic orbitals)
  - establish a way to find single-electron states and their energies
  - Humble task: aim at helium atom $\underbrace{\text{1s state}}_{\text{unknown}}$ only (thus ground state only)

[+] IPA, besides applications to atoms, is also used in understanding atomic nucleus There are Z protons & $(A-Z)$ neutrons in a nucleus. IPA gives a single-nucleon problem.

Ground state of Helium

"Two electrons in some single-electron "1s" state"

[probably you know that one in spin-up, another in spin-down]

(but it is not necessary for our purpose)

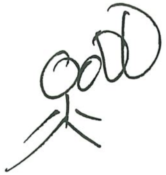
$$\psi(\vec{r}_1, \vec{r}_2) = \underbrace{\phi(\vec{r}_1) \cdot \phi(\vec{r}_2)}_{\text{unknown helium 1s state's wavefunction}} \qquad (B2)^{\dagger}$$

- Want to establish an equation to find $\phi(\vec{r})$ [note: just one function $\phi(\vec{r})$]

Consider one electron (say electron 1)

"What is the (average) effect of electron 2 on electron 1?"

[†] See Sec. F for the correct form of Eq. (B2) when spins of electrons 1 & 2 are included. Although (B2) neglected spins, the results remain valid.

Intuitively, 

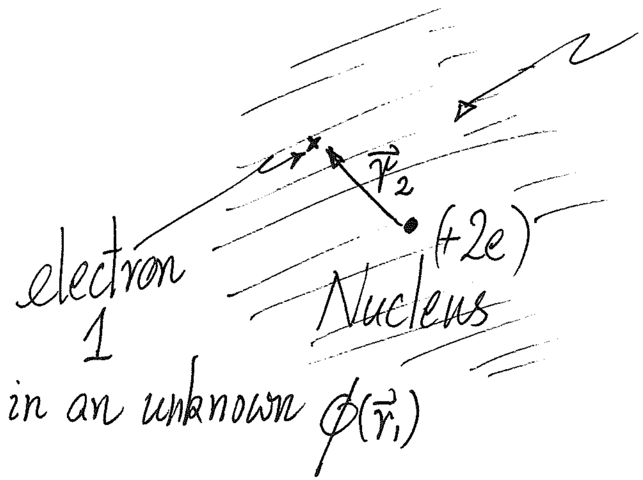
"Electron 2 in (unknown, yet-to-be-determined) ϕ, thus $\phi^*(\vec{r}_2)\,\phi(\vec{r}_2)\,d^3r_2$ is prob. of finding it at $\vec{r}_2$ in volume element d^3r_2"

- For electron 1 (we focus on) at $\vec{r}_1$, electron 2 provides a potential energy of

$$\underset{\substack{\text{on electron 1}\\ \text{due to the other}\\ \text{electron (electron 2)}}}{V_1}^{\text{eff}}(\underset{\substack{\text{coordinate}\\ \text{of electron 1}}}{r_1}) = \int \frac{\phi^*(\vec{r}_2)\,\overset{\substack{\text{but } \phi(\vec{r}) \text{ is } \underline{\text{unknown}}!}}{\phi}(\vec{r}_2)}{r_{12}}\, \underbrace{d^3r_2}_{\substack{\text{over } r_2\\ (\because\, r_1 \text{ remains})}} \quad (B3)\ [\text{atomic units}]$$

$$\underset{\underline{(\text{SI units})}}{V_1^{\text{eff}}(r_1)} = \frac{e^2}{4\pi\varepsilon_0}\int \frac{\phi^*(\vec{r}_2)\,\phi(\vec{r}_2)}{r_{12}}\, d^3r_2 \quad (B3')$$

[see Eq. (23')]



electron-electron interaction is accounted for approximately by a single-electron $V_1^{eff}(r_1)$ due to all other electrons (electron 2 here)

- An effective one-electron Schrödinger Equation-like problem to solve for $\phi(\vec{r})$

Electron 1 satisfies:

$$\boxed{\begin{aligned} &\hat{H}_1^{eff}\,\phi_{(1s)}(\vec{r}_1) = \varepsilon_{(1s)}\,\phi_{(1s)}(\vec{r}_1) \qquad (B4) \\ &\text{with} \quad \hat{H}_1^{eff}(\vec{r}_1) = -\frac{1}{2}\nabla_1^2 \overbrace{-\frac{2}{r_1}}^{\text{electron-nucleus}} + \overbrace{V_1^{eff}(r_1)}^{\text{el-el (depends on } \phi)} \qquad (B5) \end{aligned}}$$

Explicitly, Eq.(B4) & Eq.(B5) in SI units become

$$\left[-\frac{\hbar^2}{2m}\nabla^2_{\vec{r}_1} - \frac{2e^2}{4\pi\varepsilon_0 r_1} + \underbrace{\frac{e^2}{4\pi\varepsilon_0}\int \frac{\phi^*(\vec{r}_2)\,\phi(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}\, d^3r_2}_{V_1^{eff}(\vec{r}_1)}\right]\phi(\vec{r}_1) = \varepsilon_{1s}\,\phi(\vec{r}_1) \qquad (B6)$$

to solve for† $\underset{\substack{\uparrow \\ \text{[wavefunction of 1s state or } \phi_{(1s)}(\vec{r})\text{]}}}{\phi(\vec{r})}$ and ε_{1s} ← energy of 1s state

$$\hat{H}_1^{eff}\,\phi(\vec{r}_1) = \varepsilon_{1s}\,\phi(\vec{r}_1) \qquad (B7)$$

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† As we have $\phi(\vec{r})$ being the (unknown) "1s" helium atomic orbital in mind, $\phi(\vec{r})$ is $\phi_{1s}^{Helium}(\vec{r})$. We will save all the symbols for simplicity, unless necessary.

Key point to observe: Solve Eq.(B6) for $\phi_{(1s)}$ and $\varepsilon_{(1s)}$

← just one wavefunction

But $\hat{H}_1^{eff}$ in (B7) needs the unknown $\phi_{(1s)}$ to obtain V_1^{eff} !

$$\boxed{\text{Eq.(B6) and Eq.(B7) are to be solved } \underline{\text{self-consistently}} \text{ (自洽)}}$$

Key concept about IPA

① Guess a form of $\phi(\vec{r})$ ← "input"

② evaluate $V_1^{eff}(\vec{r}_1)$ [Eq.(B3')]

③ Construct $\hat{H}_1^{eff}$ and Solve Eq.(B7)

④ $\phi(\vec{r})$ is output

⑤ Compare "output" with "input"

Self-Consistent Method

$$\boxed{\text{iterate until } \phi(\vec{r}) \text{ input and } \phi(\vec{r}) \text{ output are sufficiently close}}$$

then obtain single-electron 1s state $\phi(\vec{r})$ and its energy ε_{1s} for helium

- The problem as set up in (B6)-(B7) for helium is called the Hartree approximation
- More generally (beyond ground state), we need the Hartree-Fock approximation
- All calculations are done by computers (packages)
- The methods also work for other atoms, molecules, and solids, often called self-consistent field methods
- The best value achieved by Hartree-Fock method is called the "Hartree-Fock Limit" E_{HF} (the best single-electron approximation can do)
- E_{HF} is close to but different from E_{actual} OR E_{exact}

- Helium atom

$$E_{HF}^{(GS)} = -2.8617\ E_h \quad (\text{c.f. } E_{\text{actual}} = -2.9037\ E_h)$$

(not bad!) [but not-too-good either!]

- $E_{\text{actual}} - E_{HF} \equiv$ Difference that taking the mean (smeared out) field effect of other electrons cannot account for

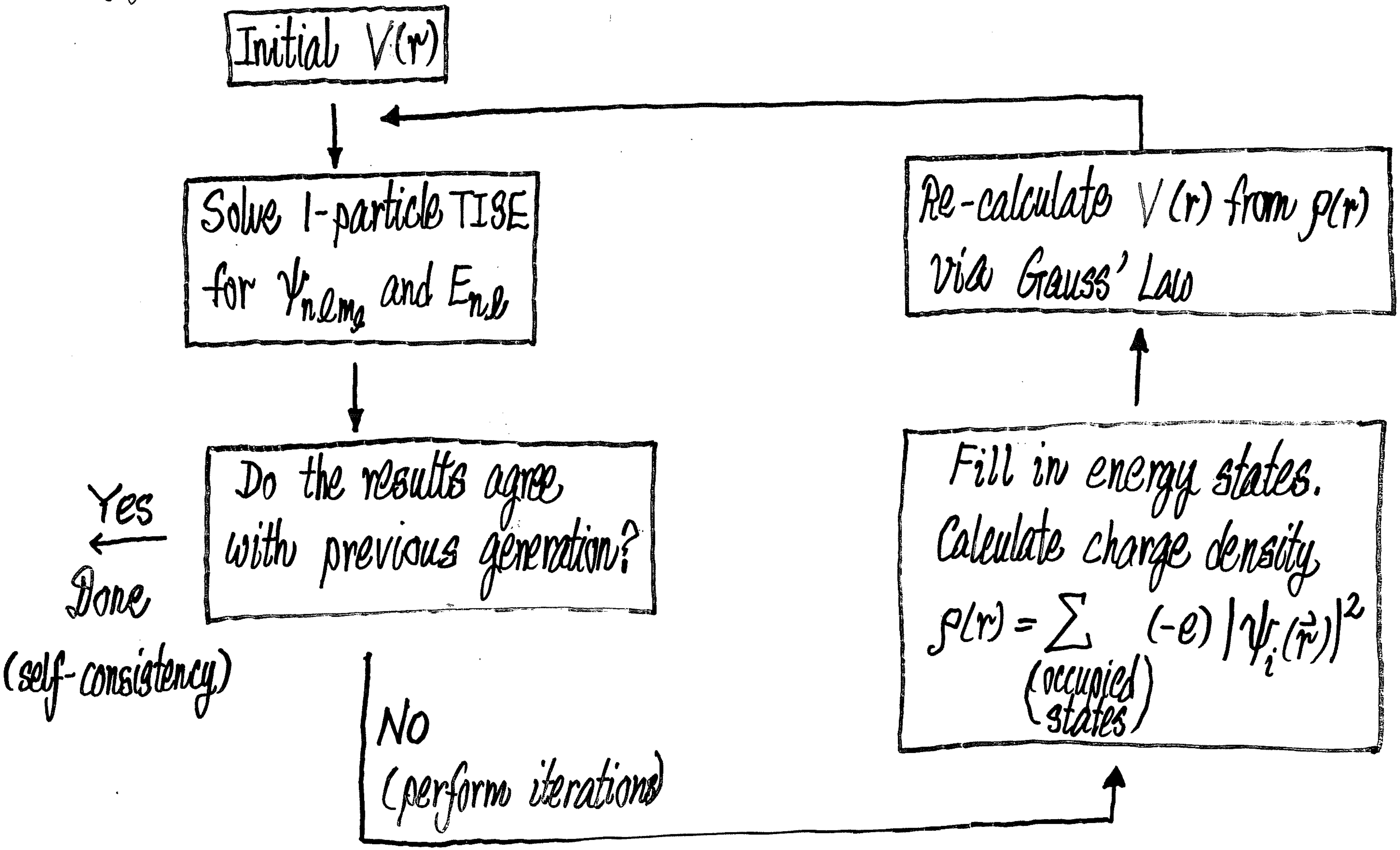
= "Correlation energy" (defines correlation energy)

∴ Correlation energy of He $= -0.0420\ E_h$

"Strongly correlated electron systems" is a hot research topic in condensed matter physics

[Meaning: Need more than Mean field Theories (Hartree-Fock)]

- Bigger Atoms (more filled states!)



Initial $V(r)$

Solve 1-particle TISE for $\psi_{n\ell m_\ell}$ and $E_{n\ell}$

Do the results agree with previous generation?

Yes ← Done (self-consistency)

No (perform iterations)

Fill in energy states. Calculate charge density

$$\rho(r) = \sum_{\text{(occupied states)}} (-e)\,|\psi_i(\vec{r})|^2$$

Re-calculate $V(r)$ from $\rho(r)$ via Gauss' Law

Hartree's self-consistent field method

- Repeat calculations for every atom

  ⇒ alignment of single-electron energy levels for an atom
- We saved the notion of 1s, 2s, 2p, 3s, 3p, 3d, … states through this journey
- At this point, we are back to the question of "how to fill electrons into single-electron states?" (see Sec. F)
- Answer leads to Pauli Exclusion Principle

  ⇒ understand periodic table!

Absolute values of one-electron energy levels in lighter atoms (in units of Hartree)

[From J. C. Slater, "Quantum Theory of Matter" (1968)]

Z	Atom		1s	2s	2p	3s	3p	3d	4s	4p
1	H	$1s$	0.500							
2	He	$1s^2$	0.8605							
3	Li	$(1s^2)2s$	2.199	0.20195						
4	Be	$(1s^2)2s^2$	4.349	0.3006						
5	B	$(1s^2)2s^22p$	7.1865	0.46195	0.2449					
6	C	$(1s^2)2s^22p^2$	10.689	0.64475	0.33015					
7	N	$(1s^2)2s^22p^3$	14.8685	0.84795	0.42225					
8	O	$(1s^2)2s^22p^4$	19.728	1.0720	0.52045					
9	F	$(1s^2)2s^22p^5$	25.269	1.31745	0.6251					
10	Ne	$(1s^2)2s^22p^6$	31.495	1.584	0.7355					
11	Na	$(1s^22s^22p^6)3s$	39.025	2.3615	1.3345	0.18885				
12	Mg	$(1s^22s^22p^6)3s^2$	47.475	3.276	2.072	0.25255				
13	Al	$(1s^22s^22p^6)3s^23p$	56.83	4.3575	2.9735	0.36225	0.1791			
14	Si	$(1s^22s^22p^6)3s^23p^2$	67.02	5.5435	3.977	0.49875	0.2401			
15	P	$(1s^22s^22p^6)3s^23p^3$	78.055	6.842	5.090	0.6294	0.30695			
16	S	$(1s^22s^22p^6)3s^23p^4$	89.945	8.255	6.314	0.7650	0.3781			
17	Cl	$(1s^22s^22p^6)3s^23p^5$	102.68	9.785	7.6515	0.9062	0.45335			
18	Ar	$(1s^22s^22p^6)3s^23p^6$	116.27	11.4325	9.1035	1.0534	0.53265			
19	K	$(1s^22s^22p^63s^23p^6)4s$	131.045	13.530	11.004	1.47605	0.8664		0.1543	
20	Ca	$(1s^22s^22p^63s^23p^6)4s^2$	146.76	15.8135	13.090	1.9375	1.24115		0.19935	
21	Sc	$(1s^22s^22p^63s^23p^6)3d4s^2$	163.145	17.9865	15.065	2.2154	1.44155	0.2654	0.21545	
22	Ti	$(1s^22s^22p^63s^23p^6)3d^24s^2$	180.385	20.2605	17.1395	2.49065	1.6830	0.31395	0.2289	
23	V	$(1s^22s^22p^63s^23p^6)3d^34s^2$	198.475	22.6445	19.323	2.76855	1.852	0.35915	0.24095	
24	Cr	$(1s^22s^22p^63s^23p^6)3d^54s$	217.225	24.9115	21.3895	2.8557	1.8455	0.23945	0.2156	
25	Mn	$(1s^22s^22p^63s^23p^6)3d^54s^2$	237.235	27.7545	24.025	3.3402	2.2388	0.44295	0.26265	
26	Fe	$(1s^22s^22p^63s^23p^6)3d^64s^2$	257.905	30.4785	26.542	3.63455	2.4456	0.48125	0.27255	
27	Co	$(1s^22s^22p^63s^23p^6)3d^74s^2$	279.445	33.324	29.179	3.93925	2.6600	0.52075	0.28235	
28	Ni	$(1s^22s^22p^63s^23p^6)3d^84s^2$	301.85	36.285	31.93	4.2500	2.878	0.55755	0.29155	
29	Cu	$(1s^22s^22p^63s^23p^6)3d^{10}4s$	324.85	39.075	34.51	4.317	2.8545	0.37155	0.25455	
30	Zn	$(1s^22s^22p^63s^23p^63d^{10})4s^2$	349.2	42.56	37.775	4.8965	3.3305	0.6291	0.30925	
31	Ga	$(1s^22s^22p^63s^23p^63d^{10})4s^24p$	374.6	46.32	41.315	5.619	3.946	1.0200	0.41885	0.18095
32	Ge	$(1s^22s^22p^63s^23p^63d^{10})4s^24p^2$	400.9	50.255	45.025	6.381	4.5985	1.44505	0.52855	0.23415
33	As	$(1s^22s^22p^63s^23p^63d^{10})4s^24p^3$	428.15	54.365	48.91	7.1875	5.2935	1.91145	0.6377	0.2913
34	Se	$(1s^22s^22p^63s^23p^63d^{10})4s^24p^4$	456.25	58.65	52.975	8.037	6.029	2.4170	0.74765	0.35075
35	Br	$(1s^22s^22p^63s^23p^63d^{10})4s^24p^5$	485.35	63.12	57.215	8.9285	6.8055	2.96225	0.85925	0.41235
36	Kr	$(1s^22s^22p^63s^23p^63d^{10})4s^24p^6$	515.3	67.765	61.625	9.864	7.6245	3.54875	0.9728	0.47595

Hartree-Fock approximation saved notion of single-electron states (atomic orbitals) for many-electron atoms

▨ These methods provide our understanding of atoms and the periodic table

Ground State Electron Configurations and Term Symbols of the Elements Hydrogen through Krypton

Z	*Atom*	*Electron configuration*	*Term symbol*
1	H	$1s$	$^2S_{1/2}$
2	He	$1s^2$	$^1S_0$
3	Li	$[He]2s$	$^2S_{1/2}$
4	Be	$[He]2s^2$	$^1S_0$
5	B	$[He]2s^22p$	$^2P_{1/2}$
6	C	$[He]2s^22p^2$	$^3P_0$
7	N	$[He]2s^22p^3$	$^4S_{3/2}$
8	O	$[He]2s^22p^4$	$^3P_2$
9	F	$[He]2s^22p^5$	$^2P_{3/2}$
10	Ne	$[He]2s^22p^6$	$^1S_0$
11	Na	$[Ne]3s$	$^2S_{1/2}$
12	Mg	$[Ne]3s^2$	$^1S_0$
13	Al	$[Ne]3s^23p$	$^2P_{1/2}$
14	Si	$[Ne]3s^23p^2$	$^3P_0$
15	P	$[Ne]3s^23p^3$	$^4S_{3/2}$
16	S	$[Ne]3s^23p^4$	$^3P_2$
17	Cl	$[Ne]3s^23p^5$	$^2P_{3/2}$
18	Ar	$[Ne]3s^23p^6$	$^1S_0$
19	K	$[Ar]4s$	$^2S_{1/2}$
20	Ca	$[Ar]4s^2$	$^1S_0$
21	Sc	$[Ar]4s^23d$	$^2D_{3/2}$
22	Ti	$[Ar]4s^23d^2$	$^3F_2$
23	V	$[Ar]4s^23d^3$	$^4F_{3/2}$
24	Cr	$[Ar]4s3d^5$	$^7S_3$
25	Mn	$[Ar]4s^23d^5$	$^6S_{5/2}$
26	Fe	$[Ar]4s^23d^6$	$^5D_4$
27	Co	$[Ar]4s^23d^7$	$^4F_{9/2}$
28	Ni	$[Ar]4s^23d^8$	$^3F_4$
29	Cu	$[Ar]4s3d^{10}$	$^2S_{1/2}$
30	Zn	$[Ar]4s^23d^{10}$	$^1S_0$
31	Ga	$[Ar]4s^23d^{10}4p$	$^2P_{1/2}$
32	Ge	$[Ar]4s^23d^{10}4p^2$	$^3P_0$
33	As	$[Ar]4s^23d^{10}4p^3$	$^4S_{3/2}$
34	Se	$[Ar]4s^23d^{10}4p^4$	$^3P_2$
35	Br	$[Ar]4s^23d^{10}4p^5$	$^2P_{3/2}$
36	Kr	$[Ar]4s^23d^{10}4p^6$	$^1S_0$

From McQuarrie "Quantum Chemistry"

Why all these?

- Some ideas on how many-electron systems can be treated
- Beginning of Computational quantum chemistry & Materials Science
- Packages for doing numerical calculations ⇒ tools available once you have the background
- See "Gaussian 2016"[+] or Gaussian.com for popular package
- Also beginning of Many-body physics (quantum field theory)
- The QM of atoms and the road to the periodic table is much more technically demanding than what you learned in secondary school and Year 1 courses

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[+] A common and professional package for computational materials science and quantum chemistry calculations.

Big Names

- John Pople / Walter Kohn⁺ (1998 Nobel Chemistry Prize)
  "for... development of computational methods in chemistry"
- J. C. Slater⁺ [1900-1976]
  - established quantum theory of atoms, molecules, solids (see his books)
  - Built up MIT's physics department
  - Slater determinant (see Sec. E), Slater orbitals

⁺ Physicists

Some further questions (optional)

- Li atom?
- Excited states of He atom?
  [Hartree-Fock approximation]

Further Reading

- D. A. McQuarrie, "Quantum Chemistry"
- S. E. Koonin, "Computational Physics"
  [there is a program for Helium atom]
- A. Modinos, "Quantum Theory of Matter"