# 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 $\underbrace{1s \text{ state}}_{\text{unknown}}$ 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)

$$\Psi(\vec{r}_1, \vec{r}_2) = \phi(\vec{r}_1) \cdot \phi(\vec{r}_2) \qquad (B2)^{\dagger}$$

$\phi$: unknown helium 1s state's wavefunction

- 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. E 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) $\phi$, 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

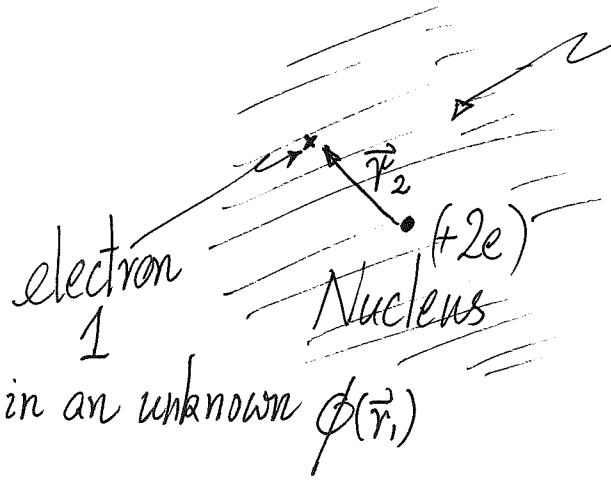
$$V_1^{eff}(r_1) = \int \frac{\phi^*(\vec{r}_2)\,\phi(\vec{r}_2)}{r_{12}}\,d^3r_2 \qquad (B3)$$

[atomic units]

- $V_1$: on electron 1 due to the other electron (electron 2)
- $r_1$: coordinate of electron 1
- $\phi^*(\vec{r}_2)\,\phi(\vec{r}_2)$: but $\phi(\vec{r})$ is unknown!
- $d^3r_2$: over $r_2$ (∴ $r_1$ remains)

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

(SI units)




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: $\hat{H}_1^{eff}\,\phi_{(1s)}(\vec{r}_1) = \mathcal{E}_{(1s)}\phi_{(1s)}(\vec{r}_1)$ (B4)

with $\hat{H}_1^{eff}(\vec{r}_1) = -\frac{1}{2}\nabla_1^2 - \underbrace{\frac{2}{r_1}}_{\text{electron-nucleus}} + \underbrace{V_1^{eff}(r_1)}_{\text{el-el (depends on } \phi)}$ (B5)

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

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

to solve for[†] $\phi(\vec{r})$ and $\mathcal{E}_{1s}$

($\phi(\vec{r})$: [wavefunction of 1s state or $\phi_{1s}(\vec{r})$]; $\mathcal{E}_{1s}$: energy of 1s state)

---

[†] As we have $\phi(\vec{r})$ being the (unknown) "1s" helium atomic orbital in mind, $\phi(\vec{r})$ is $\phi_{1s}^{\text{Helium}}(\vec{r})$. 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 (B4) needs the unknown $\phi_{(1s)}$ to obtain $V_1^{eff}$!

Eqs. (B4) and (B5) are to be solved self-consistently (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. (B4)

④ $\phi(\vec{r})$ is output

⑤ Compare "output" with "input"

Self-Consistent Method

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

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

- The problem as set up in (B4)-(B5) 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

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

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

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

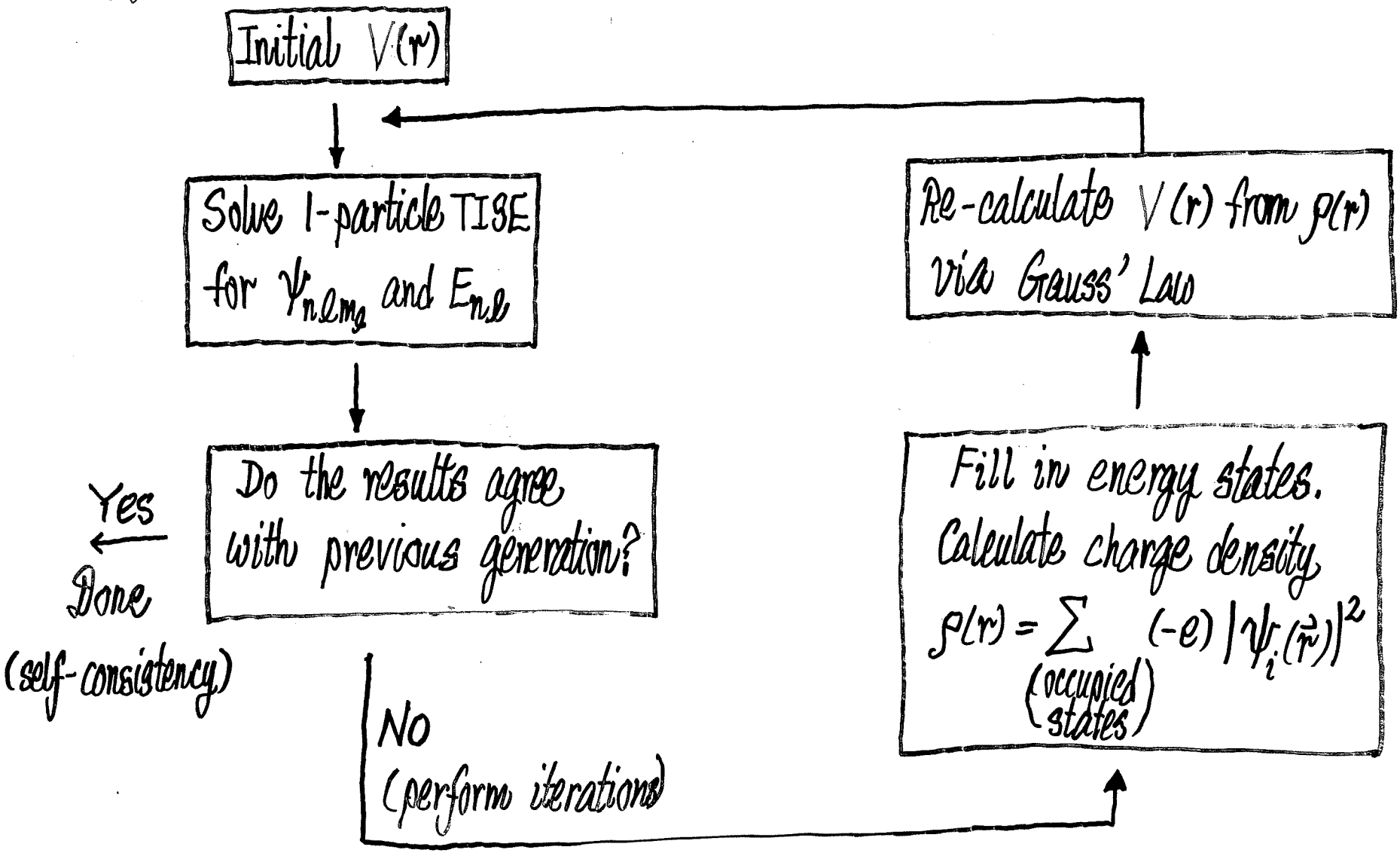
$=$ "Correlation energy" (defines correlation energy)

$\therefore$ 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!)




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. E)
- 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)]

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

| 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 |

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

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
- 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

[+] 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"