



**Short Course on
Density Functional Theory and Applications
I. Basics of Time-independent DFT**

Samuel B. Trickey

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Quantum Theory Project

Dept. of Physics and Dept. of Chemistry

trickey@qtp.ufl.edu



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Quantum Mechanics, Condensed Matter, Materials, and Chemistry

Legend:
■ Metal
■ Semimetal
■ Nonmetal

Callout for Carbon (C):
 Atomic number: 6
 Symbol: C
 Atomic weight: 12.01

1	2											13	14	15	16	17	18			
1 H 1.008												5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18			
2	3	4											11	12	13	14	15	16	17	18
3 Li 6.941	4 Be 9.012											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95			
3	4	5	6	7	8	9	10	11	12											
11 Na 22.99	12 Mg 24.31	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80			
4	5	6	7	8	9	10	11	12												
19 K 39.10	20 Ca 40.08	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3			
5	6	7	8	9	10	11	12													
37 Rb 85.47	38 Sr 87.62	71 Lu 175.0	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 209.0	85 At 210.0	86 Rn 222.0			
6	7																			
55 Cs 132.9	56 Ba 137.3																			
6	7																			
87 Fr 223.0	88 Ra 226.0																			
7																				
		6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22		
		57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 146.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0					
		89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 244.1	95 Am 243.1	96 Cm 247.1	97 Bk 247.1	98 Cf 251.1	99 Es 252.0	100 Fm 257.1	101 Md 258.1	102 No 259.1					

(c)1998
Kremer Paul

There can be no atomic shell structure in classical mechanics, so the periodic table is itself powerful testimony that QM determines chemistry, hence determines material properties.

Adapted from David Singh



Many-electron Quantum Mechanics is Challenging

**The many-electron problem in QM is difficult. What is “many”?
Here’s a table of generally solvable problems:**

Classical mechanics	Quantum mechanics	Marriage & Family	Quantum field theory
0-body	0-body	0-body	0-body
1-body	1-body	1-body	1-body
2-body	2-body	2-body ?	2-body
3-body	3-body	3-body	3-body

Credit: So Hirata

Many-electron Quantum Mechanics is Challenging (cont'd.)

- The time-independent Schrödinger equation & Hamiltonian for the N_e -electron problem with N fixed nuclei (Hartree atomic units):

$$\hat{\mathcal{H}}_{\{\mathbf{R}\}}(\mathbf{r}_1, \dots, \mathbf{r}_{N_e}) \Psi_0(\mathbf{r}_1, \sigma_1, \dots, \mathbf{r}_{N_e}, \sigma_{N_e}; \{\mathbf{R}\}) = \mathcal{E}_{0;\{\mathbf{R}\}} \Psi_0(\mathbf{r}_1, \sigma_1, \dots, \mathbf{r}_{N_e}, \sigma_{N_e}; \{\mathbf{R}\})$$

$$\begin{aligned} \hat{\mathcal{H}}_{\{\mathbf{R}\}}(\mathbf{r}_1, \dots, \mathbf{r}_{N_e}) &= -\frac{1}{2} \sum_{i=1}^{N_e} \nabla_i^2 - \sum_{i,I}^{N_e, N} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \\ &:= \sum_{i=1}^{N_e} h(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j}^{N_e} g(\mathbf{r}_i, \mathbf{r}_j) \end{aligned}$$

Sum of 1- & 2-body Hamiltonians

Nuclear positions (Born-Oppenheimer approximation);
suppressed hereafter unless directly relevant.

- Quantum chemistry (Hartree atomic units and traditional units)
vs. materials physics units (Rydberg, Hartree, & traditional units)

- **Hartree & traditional:**

$$\hbar = m_{\text{electron}} = q_{\text{electron}} = 1$$

$$1 E_{\text{Hartree}} = 27.2116 \text{ eV} \quad 1 \text{ au.} = 0.5292 \text{ \AA}$$

$$\text{One-electron KE: } -\frac{1}{2} \int d\mathbf{r} \phi \nabla^2 \phi$$

- **Rydberg & traditional units:**

$$\hbar = 2m_{\text{electron}} = q_{\text{electron}} / \sqrt{2} = 1$$

$$1 E_{\text{Rydberg}} = 13.6058 \text{ eV} \quad 1 \text{ au.} = 0.5292 \text{ \AA}$$

$$\text{One-electron KE: } -\int d\mathbf{r} \phi \nabla^2 \phi$$

Many-electron Quantum Mechanics is Challenging (cont'd.)

For a normalized ground state, the energy is therefore

$$\mathcal{E}_0 = \int \Psi_0^* (\mathbf{r}_1, \dots, \mathbf{r}_{N_e}) \hat{H} \Psi_0 (\mathbf{r}_1, \dots, \mathbf{r}_{N_e}) d\mathbf{r}_1 \dots d\mathbf{r}_{N_e}$$

$$\int \Psi_0^* (\mathbf{r}_1, \dots, \mathbf{r}_{N_e}) \Psi_0 (\mathbf{r}_1, \dots, \mathbf{r}_{N_e}) d\mathbf{r}_1 \dots d\mathbf{r}_{N_e} = 1$$

Since the state-function is anti-symmetric under particle exchange and the Hamiltonian is a symmetric sum of 1- and 2-body interactions, we end up doing integrals over all but one or two of the coordinates just to eliminate them, thus (introducing spin here):

$$\mathcal{E}_0 = \int h(\mathbf{r}_1) \gamma_{\Psi_0} (x_1 | x'_1) \Big|_{x'_1=x_1} dx_1 + \int g(\mathbf{r}_1, \mathbf{r}_2) \Gamma_{\Psi_0}^{(2)} (x_1 x_2 | x'_1 x'_2) \Big|_{\substack{x'_1=x_1 \\ x'_2=x_2}} dx_1 dx_2 \quad \leftarrow \text{Sum over spins}$$

$$\Gamma_{\Psi_0}^{(2)} (x_1 x_2 | x'_1 x'_2) := \frac{N_e (N_e - 1)}{2} \int \Psi_0^* (\mathbf{r}'_1 \sigma'_1, \mathbf{r}'_2 \sigma'_2, \mathbf{r}_3 \sigma_3, \dots, \mathbf{r}_{N_e} \sigma_{N_e}) \Psi_0 (\mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2, \mathbf{r}_3 \sigma_3, \dots, \mathbf{r}_{N_e} \sigma_{N_e}) dx_3 \dots dx_{N_e}$$

$$\gamma_{\Psi_0} (x_1 | x'_1) := N_e \int \Psi_0^* (\mathbf{r}'_1 \sigma'_1, \mathbf{r}_2 \sigma_2, \mathbf{r}_3 \sigma_3, \dots, \mathbf{r}_{N_e} \sigma_{N_e}) \Psi_0 (\mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2, \mathbf{r}_3 \sigma_3, \dots, \mathbf{r}_{N_e} \sigma_{N_e}) dx_2 dx_3 \dots dx_{N_e}$$

2-particle reduced density matrix "2-RDM"

1-particle reduced density matrix "1-RDM"

Many-electron Quantum Mechanics is Challenging (cont'd.)

$$\Gamma_{\Psi_0}^{(2)}(x_1 x_2 | x'_1 x'_2) := \frac{N_e(N_e - 1)}{2} \int \Psi_0^*(\mathbf{r}'_1 \sigma'_1, \mathbf{r}'_2 \sigma'_2, \mathbf{r}_3 \sigma_3, \dots, \mathbf{r}_{N_e} \sigma_{N_e}) \Psi_0(\mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2, \mathbf{r}_3 \sigma_3, \dots, \mathbf{r}_{N_e} \sigma_{N_e}) dx_3 \dots dx_{N_e}$$

$$\begin{aligned} \gamma_{\Psi_0}(x_1 | x'_1) &:= N_e \int \Psi_0^*(\mathbf{r}'_1 \sigma'_1, \mathbf{r}_2 \sigma_2, \mathbf{r}_3 \sigma_3, \dots, \mathbf{r}_{N_e} \sigma_{N_e}) \Psi_0(\mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2, \mathbf{r}_3 \sigma_3, \dots, \mathbf{r}_{N_e} \sigma_{N_e}) dx_2 dx_3 \dots dx_{N_e} \\ &= \frac{2}{N_e - 1} \int \Gamma^{(2)}(x_1 x_2 | x'_1 x'_2) dx_2 \end{aligned}$$

Brute force doesn't work! Suppose $N_e = 10$. Then we have to do a $3 \times 8 = 24$ - dimensional integral without coordinates 1, 2 followed by a 6-D integral involving the operator coordinates 1,2 (or some equivalent strategy).

Guessing a form for the 2-RDM and using it in the variational principle doesn't work either. This is the notorious N -representability problem. How can we know for certain that a guessed 2-RDM actually came from a properly anti-symmetric N_e particle wave function? The answer is known but using it is essentially as intractable as using the many-electron wave function.

Challenges of the QM Many-Electron Problem (continued)

Simplest physically acceptable approximate wave function is Hartree-Fock. The outline is to assume a trial variational wave-function of determinantal form:

Some assumed functional form

$$\psi(1, 2, \dots, N_e) \approx \mathcal{A} \left[\underbrace{\varphi_a(1)}_{\text{Fully coupled electrons}} \underbrace{\varphi_b(2) \cdots \varphi_z(N_e)}_{\text{Forced separation of variables = "mean field"}} \right]$$

Fully coupled electrons

Forced separation of variables = "mean field"

Antisymmetrizer

Orbital optimization

$$\Psi(1, 2, \dots, N_e) \approx A \left[\underbrace{\tilde{\varphi}_a(1)}_{\text{Variationally optimized}} \tilde{\varphi}_b(2) \cdots \tilde{\varphi}_z(N_e) \right]$$

SCF
solution

Variationally optimized

Another shorthand notation: $1 \rightarrow \mathbf{r}_1, \sigma_1$

Credit: So Hirata

Hartree-Fock: Example of Orbital Optimization by Functional Differentiation

The variational principle

$$\mathcal{E}_0 \leq \mathcal{E}_{\text{trial}} = \frac{\int \Psi_{\text{trial}}^* \hat{H} \Psi_{\text{trial}} d\mathbf{r}_1 \dots d\mathbf{r}_{N_e}}{\int \Psi_{\text{trial}}^* \Psi_{\text{trial}} d\mathbf{r}_1 \dots d\mathbf{r}_{N_e}}$$

is equivalent to the Schrödinger equation in that the S.E. arises from requiring the first variation of $\mathcal{E}_{\text{trial}}$ to be zero

$$\delta \mathcal{E}_{\text{trial}} = \frac{\delta \mathcal{E}_{\text{trial}}}{\delta \Psi_{\text{trial}}^*} \delta \Psi_{\text{trial}}^* = 0$$

$$\int \delta \Psi_{\text{trial}}^* (\hat{H} - \mathcal{E}) \Psi_{\text{trial}} d\vec{r}_1 \dots d\vec{r}_{N_e} = 0$$

$$\Rightarrow \hat{H} \Psi_0 = \mathcal{E}_0 \Psi_0$$

Lagrange Multiplier

Because of the variational principle, the H-F energy is above the true ground state energy. The task is to make the difference as small as possible by picking optimum spin-orbitals. This leads to a similar functional derivative:

$$\mathcal{E}_0 \leq \mathcal{E}_{\text{HF}} = \int \psi_{\text{HF}}^* [\{\varphi(\mathbf{r}, \sigma)\}] \hat{\mathcal{H}}(\mathbf{r}_1, \dots, \mathbf{r}_{N_e}) \psi_{\text{HF}} [\{\varphi(\mathbf{r}, \sigma)\}] d\mathbf{r}_1 \dots d\mathbf{r}_{N_e} \prod_i d\sigma_i$$

$$\frac{\delta \mathcal{E}_{\text{HF}}}{\delta \varphi_l} = 0 \quad \forall \quad l \Rightarrow \text{Variational minimum (extremum)}$$

Functional Derivatives

- A **functional** $\mathcal{F} [f]$ prescribes how to get a number, \mathcal{F} , from a function f . For example, the variational principle prescribes how to get the trial energy from the trial wave function.

- A **functional derivative** gives the change in the numerical value \mathcal{F} that depends linearly on a change in f , thus

$$\delta\mathcal{F} = \int \frac{\delta\mathcal{F}}{\delta f(\mathbf{r})} \delta f(\mathbf{r}) d\mathbf{r}$$

Analogy from ordinary calculus: differential of a function of several variables

$$dF(x_1, x_2, \dots, x_L) = \sum_{j=1}^L \frac{\partial F}{\partial x_j} dx_j$$

- The following expression will be useful in DFT. Given a functional of a function and its derivatives

$$\mathcal{F} [n, \nabla n, \nabla^2 n, \dots] := \int d\mathbf{r}' f [n(\mathbf{r}'), \nabla n(\mathbf{r}'), \nabla^2 n(\mathbf{r}'), \dots]$$

its functional derivative is

$$\frac{\delta\mathcal{F} [n, \nabla n, \nabla^2 n, \dots]}{\delta n} = \frac{\partial f(\mathbf{r})}{\partial n(\mathbf{r})} - \nabla \cdot \left(\frac{\partial f(\mathbf{r})}{\partial \nabla n(\mathbf{r})} \right) + \nabla^2 \left(\frac{\partial f(\mathbf{r})}{\partial \nabla^2 n(\mathbf{r})} \right) - + \dots$$

Challenges of the QM Many-Electron Problem (continued)

Approximate versus exact:

$$\psi(1, 2, \dots, N_e) \approx \mathcal{A}[\tilde{\varphi}_a(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(N_e)] \quad \text{HF is approximate}$$

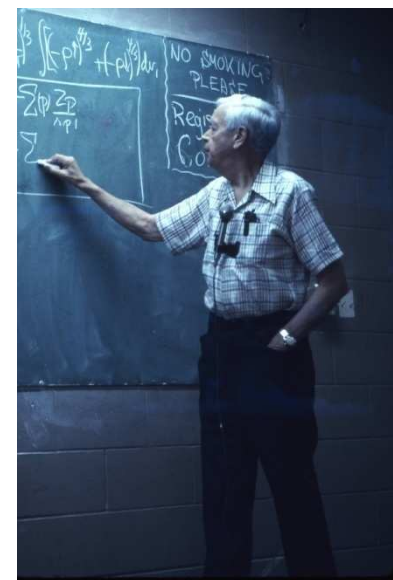
$$\Psi(1, 2, \dots, N_e) = c_0 \mathcal{A}[\tilde{\varphi}_a(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(N_e)] \quad \text{Full CI is exact}$$

All “excited” Slater
determinants →
“configuration
interaction”

$$\left\{ \begin{array}{l} +c_1 \mathcal{A}[\tilde{\varphi}_A(1)\tilde{\varphi}_b(2)\cdots\tilde{\varphi}_z(N_e)] \\ +c_2 \mathcal{A}[\tilde{\varphi}_a(1)\tilde{\varphi}_B(2)\cdots\tilde{\varphi}_z(N_e)] \\ +\dots \end{array} \right.$$

Question 1: is this expansion exact? YES

Question 2: is this expansion rapidly converging? NO



J.C. Slater (by SBT)

Credit: So Hirata

Challenges of the QM Many-Electron Problem (continued)

There is another complication! Quantum chemistry has a strange terminology for an important insight. There are two kinds of correlation contribution.

- One comes from the failure of a single Slater determinant to describe the ground state well:

$$\Psi(1, 2, \dots, N_e) = (55\%) \mathcal{A} [\tilde{\varphi}_a(1) \tilde{\varphi}_b(2) \cdots \tilde{\varphi}_z(N_e)]$$

“Non-dynamical” correlation

[coefficients arbitrary for sake of illustration]

$$\left\{ \begin{array}{l} +(30\%) \mathcal{A} [\tilde{\varphi}_A(1) \tilde{\varphi}_b(2) \cdots \tilde{\varphi}_z(N_e)] \\ +(10\%) \mathcal{A} [\tilde{\varphi}_a(1) \tilde{\varphi}_B(2) \cdots \tilde{\varphi}_z(N_e)] + \dots \end{array} \right.$$

- The other kind of correlation contribution comes from electron positions not handled properly in the mean field:

$$\Psi(1, 2, \dots, N_e) = (99\%) \mathcal{A} [\tilde{\varphi}_a(1) \tilde{\varphi}_b(2) \cdots \tilde{\varphi}_z(N_e)]$$

“Dynamical” correlation

[coefficients arbitrary for sake of illustration]

$$\left\{ \begin{array}{l} +(0.6\%) \mathcal{A} [\tilde{\varphi}_A(1) \tilde{\varphi}_b(2) \cdots \tilde{\varphi}_z(N_e)] \\ +(0.3\%) \mathcal{A} [\tilde{\varphi}_a(1) \tilde{\varphi}_B(2) \cdots \tilde{\varphi}_z(N_e)] + \dots \end{array} \right.$$

Credit: So Hirata

Limitations of Typical Wave-function Methods

Even today, many quantum chemists have a strong preference for wave-function-based, so-called “*ab initio*” methods.

Reminder: “*ab initio*” is an archaic Latin phrase meaning “expensive” (J.W.D. Connolly, about 1973)

Reminder about wave-function-based methods: Many-electron ground state is approximated by a trial wave-function:

$$\Psi \left(\{ \mathbf{R} \}; \mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2 \cdots \mathbf{r}_{N_e} \sigma_{N_e} \right)$$

Hartree Fock: Ψ is a single determinant of one-particle spin orbitals determined by variational principle. Gives bad physics for extended systems: Fermi-level pathology for metals, excessively large band gaps for insulators.

Limitations of Typical Wave-function Methods (contd.)

Various wave-function methods much-used in quantum chemistry are not feasible in surfaces, solids, immense polymers, and biomolecules because of immense computational cost.

They include

- **Configuration Interaction** – variational principle expanded in a linear combination of determinants of spin orbitals. Expensive, not size-consistent in a finite basis.
- **Many-body Perturbation Theory** (“Møller-Plesset Pert. Theory”) –
 - doesn’t converge well order by order (MBPT-2 about as good as MBPT-3 or -4)
- **Coupled Cluster Theory** - Superb accuracy, limited in practice to closed shells (the “multi-reference problem”) and about 100 electrons:

$$\Psi \left(\{ \mathbf{R} \}; \mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2 \cdots \mathbf{r}_{N_e} \sigma_{N_e} \right) = e^{\hat{T}_{cc}} \Psi_{Reference}$$

The Density (Properly, the Electron Number Density)

Can we use the density to find the ground state? Seems implausible in the face of the N -representability problem for the 2-RDM. But there is a physical argument (due to E.B. Wilson) in support of the idea.

Some preliminaries:

The [electron number] density is the “diagonal element” of the 1-RDM:

$$n_{\psi}(\mathbf{r}) = \sum_{\sigma} \gamma_{\psi}(\mathbf{r}\sigma | \mathbf{r}\sigma) \quad (\text{chemists use symbol } \rho)$$

$$\gamma_{\psi}(x_1 | x'_1) := N_e \int \psi^*(\mathbf{r}'_1 \sigma'_1, \mathbf{r}_2 \sigma_2, \mathbf{r}_3 \sigma_3, \dots, \mathbf{r}_{N_e} \sigma_{N_e}) \psi(\mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2, \mathbf{r}_3 \sigma_3, \dots, \mathbf{r}_{N_e} \sigma_{N_e}) dx_2 dx_3 \dots dx_{N_e}$$

$$x_i := \mathbf{r}_i, \sigma_i$$

Note that the probability of finding an electron at position \mathbf{r} is $N_e^{-1} n_{\psi}(\mathbf{r})$

and that
$$\int d\mathbf{r} n_{\psi}(\mathbf{r}) = N_e$$

The spin density is $n_{\psi}(\mathbf{r}\sigma) = \gamma_{\psi}(\mathbf{r}\sigma | \mathbf{r}\sigma)$

The total density is $n_{\psi}(\mathbf{r}) = n_{\psi}(\mathbf{r}\alpha) + n_{\psi}(\mathbf{r}\beta)$

E.B. Wilson's Argument

1. We know we are dealing with electrons (back to the periodic table argument), so we know the form of the Hamiltonian.

2. If we know the electron number density at all points in space, we can get the number of electrons: $\int dr n(\mathbf{r}) = N_e$

3. In the neighborhood of nucleus I , the Kato cusp condition gives:

$$n(\mathbf{r}) \sim 1 - 2Z_I |\mathbf{r}| + O(|\mathbf{r}|^2)$$

so the density $n(\mathbf{r})$ identifies the location and charge of every nucleus.

4. Therefore, knowledge of the density $n(\mathbf{r})$ is equivalent to knowing all the system-dependent constants in the many-electron Hamiltonian

$$\hat{\mathcal{H}}_{\{\mathbf{R}\}}(\mathbf{r}_1, \dots, \mathbf{r}_{N_e}) = -\frac{1}{2} \sum_{i=1}^{N_e} \nabla_i^2 - \sum_{i,I}^{N_e, N} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} := \sum_{i=1}^{N_e} h(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j}^{N_e} g(\mathbf{r}_i, \mathbf{r}_j)$$

5. Since the many-electron Hamiltonian determines the ground state, it follows that the density determines the ground state.

Rudiments of Density Functional Theory

Hohenberg-Kohn Theorems – consider the N_e -electron Hamiltonian, which includes an external potential (for us, the nuclear-electron attraction)

$$\begin{aligned}\hat{\mathcal{H}}_{\{\mathbf{R}\}}(\mathbf{r}_1, \dots, \mathbf{r}_{N_e}) &= -\frac{1}{2} \sum_{i=1}^{N_e} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I}^{N_e, N} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \\ &:= \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} + \hat{\mathcal{V}}_{ext} \equiv \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} + \hat{\mathcal{V}}_{Nuc-electr}\end{aligned}$$

HK-I: “A given ground state density $n_0(\mathbf{r})$ determines the ground state wave function and hence all the ground state properties of an N_e -electron system.”

Original Proof: by contradiction [P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964)]

Modern Proof: Levy-Lieb constrained search (sequential application of the Variational Principle density by density)

[M. Levy, Proc. Natl. Acad. Sci. USA 76, 6062 (1979); L. Lieb, Internat. J. Quantum Chem. 24, 243 (1983)]

HK-I Proof by Contradiction

1. Consider a non-degenerate ground state. Suppose that there are two external potentials that yield the same ground-state density:

$$\hat{v}_{ext}, \hat{v}'_{ext} \mapsto n_0$$

2. Then by the variational principle

$$\begin{aligned}\mathcal{E}'_0 &= \langle \Psi'_0 | \hat{\mathcal{H}}' | \Psi'_0 \rangle < \langle \Psi_0 | \hat{\mathcal{H}}' | \Psi_0 \rangle = \langle \Psi_0 | \hat{\mathcal{H}} + \hat{v}'_{ext} - \hat{v}_{ext} | \Psi_0 \rangle \\ &= \mathcal{E}_0 + \langle \Psi_0 | \hat{v}'_{ext} - \hat{v}_{ext} | \Psi_0 \rangle = \mathcal{E}_0 + \int d\mathbf{r} n(\mathbf{r}) [v'_{ext}(\mathbf{r}) - v_{ext}(\mathbf{r})]\end{aligned}$$

3. But the argument can be done reversing primed and unprimed quantities.

This gives

$$\mathcal{E}_0 = \mathcal{E}'_0 + \int d\mathbf{r} n(\mathbf{r}) [v_{ext}(\mathbf{r}) - v'_{ext}(\mathbf{r})]$$

4. Adding these last two results gives the contradiction $\mathcal{E}_0 + \mathcal{E}'_0 < \mathcal{E}_0 + \mathcal{E}'_0$

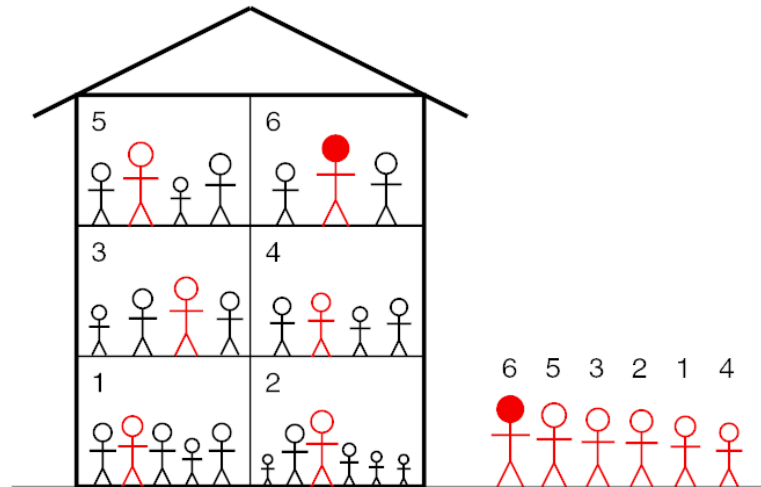
5. Therefore the ground state density determines the external potential and hence, the ground state wave function.

Remark: this proof does not address the possibility of a density n which is not associated with any v_{ext} (the v -representability problem)

Constrained Search [Parr and Yang; Fig. 3.1(b), p. 59]

Suppose there is an elementary school with six classrooms, 1st through 6th Grade. How could one find the tallest pupil and know his/her identity?

- The “Rayleigh-Ritz variational approach”: gather all the pupils (*e.g., in the cafeteria*) and measure each. Keep a record of the greatest height found so far, along with the name and grade of that pupil. Except for “degeneracies” (students of the same height), that record never would contain more than one name.
- The “constrained search approach”: search each grade for the tallest student in that room, then combine the results into a single list and search that for the tallest member. If the list has more than 6 entries, then those sets of students who have the same height belong to *equivalence classes*.



credit N. Rösch

HK-I Proof by Constrained Search

1. Consider the positive operator $\hat{T} + \hat{V}_{ee}$ and form

$$\mathcal{E}[\psi] = \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle$$

2. Minimize this functional over all the N_e electron states that give n_0

$$\begin{aligned} \mathcal{E}[\psi_0] &= \min_{\psi} \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle \\ &\ni \gamma_{\psi}(\mathbf{r} | \mathbf{r}) = n_0(\mathbf{r}) \end{aligned}$$

3. Then at most ψ_0 is a normalized linear combination of ground states, since the external potential contribution to the total energy depends only on the density:

$$\mathcal{E}_{ext} = \int d\mathbf{r} n_0(\mathbf{r}) v_{ext}(\mathbf{r})$$

4. Therefore the ground state density determines the ground state wave function.

Remarks: No v -representability problem, no restriction to non-degenerate ground states. We have not shown that, subject to mild conditions, every density is associated with at least one N_e electron state. In fact, there are infinitely many such states for each density (Harriman, Phys. Rev. A 24, 680 (1981)).

Rudiments of DFT (continued)

HK-II: “For an N_e –electron system with an external potential $v_{ext}(\mathbf{r})$, there exists a universal (*i.e.*, independent of v_{ext}) functional $F[n]$ with the following properties:

$$E_{v_{ext}}[n] = F[n] + \int d\mathbf{r} n(\mathbf{r}) v_{ext}(\mathbf{r}) \geq E_0$$

$$E_{v_{ext}}[n_0] = E_0 = \min_{n(\bar{r})} E_{v_{ext}}[n] \quad \forall \text{ physically acceptable } n(\mathbf{r})$$

Original Proof: Essentially by announcement; the paper assumes that HK-I holds for non-ground-state densities.

Modern Proof: Levy-Lieb Constrained Search

Form
$$F[n] := \min_{\psi \mapsto n} \langle \psi | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \psi \rangle \equiv \langle \psi_{min;n} | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \psi_{min;n} \rangle$$

Then

$$E_0 = \langle \Psi_0 | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} + \hat{\mathcal{V}}_{ext} | \Psi_0 \rangle \leq \langle \psi_{min;n} | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} + \hat{\mathcal{V}}_{ext} | \psi_{min;n} \rangle$$

$\hookrightarrow = F[n] + \int d\mathbf{r} n(\mathbf{r}) v_{ext}(\mathbf{r}) := E_{v_{ext}}[n]$

which is the first piece of the theorem.

HK-II proof (continued)

Now apply the variational principle again

$$E_0 = \langle \Psi_0 | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} + \hat{\mathcal{V}}_{ext} | \Psi_0 \rangle \leq \langle \psi_{min;n_0} | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} + \hat{\mathcal{V}}_{ext} | \psi_{min;n_0} \rangle$$
$$\Rightarrow \langle \Psi_0 | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \Psi_0 \rangle \leq \langle \psi_{min;n_0} | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \psi_{min;n_0} \rangle$$

But the definition of $\psi_{min;n}$ means that $\langle \psi_{min;n_0} | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \psi_{min;n_0} \rangle \leq \langle \Psi_0 | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \Psi_0 \rangle$

Taken together, these give bracketing inequalities

$$\langle \Psi_0 | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \Psi_0 \rangle \leq \langle \psi_{min;n_0} | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \psi_{min;n_0} \rangle = F[n_0] \leq \langle \Psi_0 | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \Psi_0 \rangle$$
$$\Rightarrow F[n_0] = \langle \Psi_0 | \hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee} | \Psi_0 \rangle \Rightarrow E_{v_{ext}}[n_0] = E_0$$

Remark: This $F[n]$ is NOT the same mathematical object as the one originally defined by HK. In particular, there is no ν -representability issue with regard to the variation over n nor restriction to non-degenerate ground state. This functional does fulfill the role of the one defined by HK.

Bijjective mapping

The original proof by contradiction of HK-I establishes a bijective mapping between $n(\mathbf{r})$ and $v_{ext}(\mathbf{r})$. The Levy-Lieb constrained search seems to lose that but, at least formally, the ground state part can be recovered.

Assume that n_0 and Ψ_0 been found as the minimum of

$$F[n] + \int d\mathbf{r} n(\mathbf{r}) v_{ext}(\mathbf{r})$$

Then

$$\Psi_0 = \Psi_0[n_0] \text{ and } E_0 = E_0[n_0]$$

$$\Rightarrow \hat{\mathcal{V}}_{ext} \Psi_0[n_0] = E_0[n_0] \Psi_0[n_0] - (\hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee}) \Psi_0[n_0]$$

$$\hat{\mathcal{V}}_{ext} = E_0[n_0] - \frac{1}{\Psi_0[n_0]} (\hat{\mathcal{T}} + \hat{\mathcal{V}}_{ee}) \Psi_0[n_0]$$