Lecture 10 Density Functional Theory

Single and pair electron densities; exchange and Coulomb correlation; hole functions; Hohenberg-Kohn theorems

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The *electron density* is a marginal probability obtained from the full *n*-electron distribution

$$\hat{
ho}^{s}(\mathbf{r}) = N^s \int \ldots \int |\Psi(au, au_2,\ldots, au_N)|^2 d au_2\ldots d au_N$$

- All electrons are equivalent, so singling out the first one does not restrict the generality of the definition
- A function of just 3 spatial variables (x, y, z)

- Normalizes to N^s : $\rho^s(\mathbf{r})d\mathbf{r} = N^s$

ρ(r) has a finite cusp at the atom nuclei

onin

• Decays exponentially away from all nuclei

Also spin-averaged density $ho({f r})=
ho^{\uparrow}({f r})+
ho^{\downarrow}({f r})$

If ψ is given by a Slater determinant, $\rho(r)$ is a sum of the orbital electron densities

$$ho({f r})=\sum_i n_i |\phi_i({f r})|^2$$

nM = 3:

```
tauList0 = ToExpression["t" <> ToString[#] & /@ Range[nM]]

#[tau_List] := With[{n = Length[tau]},

1

Sqrt[n1] Det[Table[$$;[tau[j]], {j, n}, {i, n}]]]

BraKet[{f_[t1] q_}, {$[t1] r_}] :=

f[t1] *$g[t1] *BraKet[{q}, {r}]

#[tauList0]

nM BraKet[{$[tauList0]}, {$[tauList0]]];

* /. orthonormalRule // Simplify

{t1, t2, t3}

<math>\frac{1}{\sqrt{6}} (-\phi_1[t3] \phi_2[t2] \phi_3[t1] + \phi_1[t2] \phi_2[t3] \phi_3[t1] + \phi_1[t3] \phi_2[t1] \phi_3[t2] - \phi_1[t1] \phi_2[t2] \phi_3[t3])

\phi_1[t2] \phi_2[t1]^2 + \phi_2[t1]^2 + \phi_3[t1]^2
```

The electron pair density is important for understanding electron correlation

$$ho_2^{s_1,s_2}({f r}_1,{f r}_2) = N^{s_1}(N^{s_2}-\delta_{s_1,s_2})\int \ldots \int |\Psi(au_1, au_2,\ldots, au_N)|^2 d au_3\ldots d au_N$$

- For uncorrelated electrons: $\rho_2^{s_1,s_2}(\mathbf{r}_1,\mathbf{r}_2) = \frac{N-1}{N}\rho^{s_1}(\mathbf{r}_1)\rho^{s_2}(\mathbf{r}_2)$
 - same electron can't contribute to both $\rho(1)$ and $\rho(2)$

- But electrons are strongly correlated
 - Pauli exclusion

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- Coulomb repulsion
- Consider the *reduced density matrix* for two electrons

 $\gamma_2(1,2,1',2') = N(N-1)\int \ldots \int \Psi^*(1,2,\ldots,N)\Psi(1',2',\ldots,N)d3\ldots dN$ For this development, these include spin coordinates too

switching to simpler notation when meaning isn't ambiguous

Application of the Pauli principle to y leads to Pauli exclusion *at a point in space*

 $\gamma_2(1,2,1',2') = N(N-1) \int \ldots \int \Psi^*(1,2,\ldots,N) \Psi(1',2',\ldots,N) d3\ldots dN$

• Swapping 1 and 2 (or 1' and 2') changes sign of γ_2

$$\gamma_2(2,1,1',2')=-\gamma_2(1,2,1',2')$$

• The "diagonal elements" (x' = x) are the pair density

$$\gamma_2(2,1,1,2)=-\gamma_2(1,2,1,2)=-
ho^{s_1,s_2}(1,2)$$

• But also, when 1 = 2, electrons have same spin and location

$$ho^{s_1,s_1}(1,1)=\gamma_2(1,1,1,1)=-\gamma_2(1,1,1,1)=-
ho^{s_1,s_1}(1,1)$$

• Pair density must be zero \rightarrow cannot occupy same location

Electrons of the same spin do not move independently: *Fermi*, or *exchange correlation* $\rho_2^{s,s}(1,1) = 0$

- Effect has nothing (yet) to do with Coulomb interaction
- Effect does not apply to electrons of different spin
- A Slater determinant captures this effect

 $\Psi(1,2) = rac{1}{\sqrt{2}} egin{pmatrix} \phi_1({f r}_1)\sigma_1(s_1) & \phi_2({f r}_1)\sigma_2(s_1) \ \phi_1({f r}_2)\sigma_1(s_2) & \phi_2({f r}_2)\sigma_2(s_2) \end{pmatrix}$

$$ho_2(1,2) = \sum_{s_1,s_2} \Psi^*(1,2) \Psi(1,2)$$



Electrostatic repulsion is another source of correlation: *Coulomb*, or just *electron correlation*

- Slater determinant does not capture this at all
 - For opposite spins, pair density is a product of singlet densities

$$egin{aligned}
ho_2(1,2) &= \sum_{s_1,s_2} \left(rac{1}{\sqrt{2}} igg| egin{pmatrix} \phi_1(\mathbf{r}_1) \sigma_1(s_1) & \phi_2(\mathbf{r}_1) \sigma_2(s_1) \ \phi_1(\mathbf{r}_2) \sigma_1(s_2) & \phi_2(\mathbf{r}_2) \sigma_2(s_2) \ \end{pmatrix}
ight) \ &= rac{1}{2} igg(\phi_1(2)^2 \phi_2(1)^2 + \phi_1(1)^2 \phi_2(2)^2 igg) \ &= rac{1}{2} ig(
ho_{\phi_1}(2)
ho_{\phi_2}(1) +
ho_{\phi_1}(1)
ho_{\phi_2}(2) igg) \end{aligned}$$

The *exchange-correlation hole* is the difference between correlated and uncorrelated densities



$$ho_2(1,2)=
ho(1)
ho(2)+
ho(1)h_{
m XC}(1,2)$$

- Presence of electron 1 typically depletes the probability of electron 2, hence the description of this as a "hole"
- Integrated over all space, the hole is -1

$$\int h_{
m XC}(1,2)d2=-1$$

$$\int
ho_2(1,2)d2 = (N-1)
ho(1) \ \int
ho(2)d2 = N$$

Knowledge of $h_{\rm XC}$ can be used to correct the classical electron-electron electrostatic energy



- The second term is the interaction of the charge density with the Coulomb-exchange hole
- Its contribution is negative in general, so the chargedensity/hole interaction is favorable
- Consider separate Coulomb and Fermi terms: $h_{\rm XC} = h_X^{s_1=s_2} + h_C^{s_1,s_2}$

Is their reason to believe that the electron density ρ is sufficient to do quantum chemistry?

- Yes. Note these observations:
 - The Hamiltonian is uniquely defined by
 - Number of electrons, N
 - Positions of nuclei, R_A
 - The charges of the nuclei, Z_A
 - The electron density has the same information
 - $\int
 ho(1)d1 = N$
 - Cusps in *p* locate the positions of the nuclei
 - There is also a relation between the ho and Z_A: $\lim_{r_{iA} \to 0} \left| \frac{\partial}{\partial r} + 2Z_{\rm A} \right|
 ho({f r}) = 0$
- Given the electron density, a Hamiltonian could be defined, so all the relevant information is there

Why would we prefer to work with the electron density rather than the wavefunction?

- Wavefunction
 - Contains all information about the system
 - It's exact specification is given by the Schrödinger equation
 - We can obtain any observable property from it
 - Complicated, 4N-dimensional function
 - Must satisfy Pauli principle
 - Cannot be probed experimentally
 - Hard to think about intuitively
- Electron density
 - Has the necessary information
 - 3-dimensional function, regardless of N
 - Can be measured experimentally
 - We don't know how to evaluate it directly (i.e., without evaluating the wavefunction) and exactly for a given set of nuclei

The Hohenberg-Kohn theorems provide a rigorous basis for using $\rho(r)$ to do quantum chemistry

• First theorem: proof of existence

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- The external potential $V_{\text{ext}}(\mathbf{r})$ (i.e., due to the nuclei) is a unique functional of the electron density $\rho(\mathbf{r})$
 - I.e., only one $V_{\text{ext}}(\mathbf{r})$ yields a ψ from the SE that has density $\rho(\mathbf{r})$
- Inasmuch as $V_{\text{ext}}(\mathbf{r})$ (plus kinetic and e-e energies) defines the Hamiltonian, we conclude that the ground-state energy E_0 is also determined uniquely by $\rho(\mathbf{r})$
- In short, there exists a functional that yields the ground-state energy for a given electron density, $E_0[\rho]$ Functional: plug in a function, get a number. E.g.

 $\mathcal{F}[f]=\int^1 f(x)dx$

- We want to choose $V_{\text{ext}}(\mathbf{r})$, not $\rho(\mathbf{r})$, so we'll have to turn this around eventually

The *reductio ad absurdum* HK proof of existence is surprisingly simple

- Assume two different external potentials $V_{\text{ext},1}$ and $V_{\text{ext},2}$ both give rise to the same $\rho(\mathbf{r})$ from their wavefunctions ψ_1 and ψ_2
- Their Hamiltonians, \hat{H}_1, \hat{H}_2 , differ only by $V_{\text{ext},2}$ - $V_{\text{ext},1}^{\hat{H}=\hat{T}+\hat{V}_{\text{ee}}+\hat{V}_{\text{ext}}}$
- Consider (E) from swapping wavefunctions

$$egin{aligned} &\langle E_0
angle_1 < \left\langle \Psi_2 | \hat{H}_1 | \Psi_2
ight
angle = \left\langle \Psi_2 | \hat{H}_2 | \Psi_2
ight
angle + \left\langle \Psi_2 | \hat{V}_{\mathrm{ext},1} - \hat{V}_{\mathrm{ext},2} | \Psi_2
ight
angle \ & \mathcal{R}_{\mathrm{epeat,}} &\langle E_0
angle_1 < \langle E_0
angle_2 + \int
ho(\mathbf{r})(V_{\mathrm{ext,1}}(\mathbf{r}) - V_{\mathrm{ext,2}}(\mathbf{r})) d\mathbf{r} \ & \mathcal{R}_{\mathrm{epeat,}} &\langle E_0
angle_1 < \langle E_0
angle_2 < \langle E_0
angle_1 + \int
ho(\mathbf{r})(V_{\mathrm{ext,2}}(\mathbf{r}) - V_{\mathrm{ext,1}}(\mathbf{r})) d\mathbf{r} \ & \mathcal{R}_{\mathrm{ext,2}} &\langle E_0
angle_1 + \langle E_0
angle_2 < \langle E_0
angle_2 + \langle E_0
angle \ & \mathcal{R}_{\mathrm{ext,2}}(\mathbf{r}) - V_{\mathrm{ext,1}}(\mathbf{r})) d\mathbf{r} \ & \mathcal{R}_{\mathrm{ext,2}} &\langle E_0
angle_1 + \langle E_0
angle_2 < \langle E_0
angle_2 + \langle E_0
angle \ & \mathcal{R}_{\mathrm{ext,2}}(\mathbf{r}) - V_{\mathrm{ext,1}}(\mathbf{r})) d\mathbf{r} \ & \mathcal{R}_{\mathrm{ext,2}} &\langle E_0
angle_1 + \langle E_0
angle_2 < \langle E_0
angle_2 + \langle E_0
angle_2 \ & \mathcal{R}_{\mathrm{ext,2}}(\mathbf{r}) - V_{\mathrm{ext,1}}(\mathbf{r}) \ & \mathcal{R}_{\mathrm{ext,2}}(\mathbf{r}) + \langle E_0
angle_2 + \langle E_0
angle_2 \ & \mathcal{R}_{\mathrm{ext,2}}(\mathbf{r}) + \langle E_0
angle_2 \ & \mathcal{R}_{\mathrm{ext,2}}(\mathbf{r}) \ & \mathcal{R}_{\mathrm{ext,2}}(\mathbf{r}$$

The HK theorem says nothing about the form of the energy functional

• We can separate the energy into pieces and consider each:

electron-

$$E_0[
ho]=T[
ho]+E_{
m ee}[
ho]+E_{
m Ne}[
ho]$$

electron-

• We can evaluate or estimate some parts

kinetic

 $E_0 \equiv \langle E_0
angle$

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$$E_{
m Ne}[
ho] = \int
ho(\mathbf{r}) V_{
m Ne}(\mathbf{r}) d\mathbf{r}$$

 $E_{
m ee}[
ho] = rac{1}{2} \int \int rac{
ho(\mathbf{r}_1)
ho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 \mathbf{r}_2 + E_{
m ncl}[
ho]$
classical classical; corrects for self-interaction and exchange and Coulomb correlation

• Devising functionals for T and E_{ncl} is the central problem of electronic density functional theory

The second HK theorem addresses the need to specify $V_{ext}(r)$ independently, rather than $\rho(r)$

- Given $V_{\text{ext}}(\mathbf{r})$, the density ρ_0 that minimizes $E_0[\rho]$ is the true electron density for that potential
- We solve for $\rho(\mathbf{r})$ again with a variational principle!
- Proof:

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– Any trial ρ' corresponds to a trial V'_{ext} and hence a trial H' and ψ'

$$ig\langle \Psi' | \hat{H} | \Psi' ig
angle \geq ig\langle \Psi | \hat{H} | \Psi ig
angle = E_0[
ho_0]$$
Hamiltonian for desired $V_{ ext{ext}}$

- Energy of the *trial* ψ with the *target H* is minimum only when it is the ψ for that *H*, and that happens only when ρ is the density for that *H*

HK variational principle is not as powerful as the wavefunction-based statement

- HK variational principle applies to the exact energy functional
 - We have only an approximation to this functional
 - Minimization may not take us to the correct electron density
 - Minimized energy may be lower than true ground-state energy
- In wavefunction theories, we know the exact expectation energy for a given wavefunction $\langle E \rangle = \langle \Psi | \hat{H} | \Psi \rangle$
 - Minimization certainly brings us closer to the correct wavefunction
 - Minimum will not be lower than true ground-state energy

Summary

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- Singlet and pair densities convey coarse-grained information about the electron distributions, and are much simpler than the wavefunction
- The HK theorems show that the singlet density in principle contains all the information needed to obtain a full description of the system
- This information is represented as a functional of the density
 We don't know form of this functional this is the next step
- A variational principle guides evaluation of the electron density for a given molecular system

Suggested Reading/Viewing

- Wolfram Koch and Max C. Holthausen, *A Chemist's Guide to Density Functional Theory*, 2nd ed., Wiley (2001)
 - Chapters 2, 3, 4
 - On digital reserve at the UB library <u>https://search.lib.buffalo.edu/permalink/01SUNY_BUF/9qhqtp/alma990021458730204803</u>
- David S. Sholl and Janice A. Steckel, *Density Functional Theory: A Practical Introduction*, Wiley (2009).
 - Available online via UB library: https://search.lib.buffalo.edu/permalink/01SUNY_BUF/9qhqtp/alma9938803702004803
 - Chapter 1
- Autschbach, Sec. 8.6
- Cramer
 - Video 5.01: <u>https://www.youtube.com/watch?v=ofyr1GyEZsU</u>
 - Video 5.02: <u>https://www.youtube.com/watch?v=hrpfTvrI2s4</u> (note erratum video that follows it)
 - Video 5.03: <u>https://www.youtube.com/watch?v=vvRS8SHjAFw</u>