## Review of Electronic Structure Methods



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## An (un)attainable goal?

## $\hat{H} \Psi=E \Psi$


"Big data meets quantum chemistry approximations: The Delta-machine learning approach". Ramakrishnan et al. J. Chem. Theor. Comput. 11, 2087 (2015).
"Machine learning for manybody physics: The case of the Anderson impurity model" Louis-Francois et al. Phys. Rev. B 90155136 (2014).
"Solving the quantum manybody problem with artificial neural networks"
Carleo and Troyer Science 355, 602 (2017).
"Bypassing the Kohn-Sham equations with machine learning", Brockherde et al. Nature Comm. (in review).

## The "Universal" Hamiltonian

$M$ Electrons
$N$ Nuclei

$$
\hat{H}=\hat{\hat{C}}_{c}+\hat{Y}_{n}+\hat{V}_{c e}+\hat{V}_{c n}+\hat{V}_{m n}
$$

## Operator Definitions:

Electronic:

$$
\begin{aligned}
& \hat{T}_{e}=-\frac{1}{2} \sum_{i=1}^{M} \nabla_{i}^{2} \\
& \hat{V}_{e e}=\sum_{i>j}^{M} \frac{1}{\left|\hat{\mathbf{r}}_{i}-\hat{\mathbf{r}}_{j}\right|}
\end{aligned}
$$

Nuclear:

$$
\begin{gathered}
\hat{T}_{n}=-\frac{1}{2} \sum_{I=1}^{N} \frac{1}{M_{I}} \nabla_{I}^{2} \\
\hat{V}_{n n}=\sum_{I>I}^{N} \frac{Z_{I} Z_{J}}{\left|\hat{\mathbf{R}}_{I}-\hat{\mathbf{R}}_{J}\right|}
\end{gathered}
$$

Coupling:

$$
\hat{V}_{e n}=-\sum_{i=1}^{M} \sum_{l=1}^{N} \frac{Z_{l}}{\left|\frac{\mathbf{r}_{i}}{}-\hat{\mathbf{R}}_{l}\right|}
$$

## Molecular energy levels

Electron coordinates
Notation:

$$
\begin{aligned}
& \mathbf{r} \\
= & \mathbf{r}_{1}, \ldots, \mathbf{r}_{M} \\
\mathbf{x} & =\mathbf{r}_{1}, s_{z, 1}, \ldots, \mathbf{r}_{M}, s_{z, M} \\
s_{z, i}=\uparrow, & \alpha,\binom{1}{0} \text { or } \downarrow, \beta,\binom{0}{1}
\end{aligned}
$$

Complete energy level spectrum:

$$
\hat{H} \Psi(\mathbf{x}, \mathbf{R})=E \Psi(\mathbf{x}, \mathbf{R})
$$

$$
\left[\hat{T}_{e}+\hat{T}_{n}+V_{e e}(\hat{\mathbf{r}})+V_{e n}(\hat{\mathbf{r}}, \hat{\mathbf{R}})+V_{n n}(\hat{\mathbf{R}})\right] \Psi(\mathbf{x}, \mathbf{R})=E \Psi(\mathbf{x}, \mathbf{R})
$$

## Born-Oppenheimer Approximation

à la W. H. Flygare, Molecular Structure and Dynamics

$$
\text { Mass disparity: } M_{\mathrm{H}^{+}} \approx 2000 m_{e}
$$

Quasi adiabatic separability ansatz for wave function:

$$
\Psi(\mathbf{x}, \mathbf{R})=\varphi(\mathbf{x}, \mathbf{R}) \chi(\mathbf{R})
$$

Schrödinger equation separates if

$$
\nabla_{I} \chi(\mathbf{R}) \gg \nabla_{I} \varphi(\mathbf{x}, \mathbf{R})
$$



Electrons in fixed background nuclear geometry $\mathbf{R}$

$$
\left[\hat{T}_{e}+\hat{V}_{e e}(\hat{\mathbf{r}})+\hat{V}_{e n}(\hat{\mathbf{r}}, \mathbf{R})\right] \varphi_{\alpha}(\mathbf{x}, \mathbf{R})=\varepsilon_{\alpha}(\mathbf{R}) \varphi_{\alpha}(\mathbf{x}, \mathbf{R})
$$

Nuclei on each electronic hypersurface

$$
\left[\hat{T}_{n}+\varepsilon_{\alpha}(\hat{\mathbf{R}})+\hat{V}_{n n}(\hat{\mathbf{R}})\right] \chi_{v}(\mathbf{R})=E_{v} \chi_{v}(\mathbf{R})
$$

Born-Oppenheimer (electronic) surfaces and nuclear energy levels


## Classical nuclear motion on an electronic surface

Consider the ground-state electronic surface $\varepsilon_{0}(\mathbf{R})$

Nuclear Hamiltonian:

$$
\hat{\mathcal{H}}=\hat{T}_{n}+\varepsilon_{0}(\hat{\mathbf{R}})+V_{n n}(\hat{\mathbf{R}})
$$

"Demote" to a classical Hamiltonian:

$$
\mathcal{H}(\mathbf{P}, \mathbf{R})=\sum_{I=1}^{N} \frac{\mathbf{P}_{I}^{2}}{2 M_{I}}+\varepsilon_{0}(\mathbf{R})+V_{n n}(\mathbf{R})
$$

Nuclear motion now given by Hamilton's equations:

$$
\dot{\mathbf{R}}_{I}=\frac{\mathbf{P}_{I}}{M_{I}} \quad \dot{\mathbf{P}}_{I}=-\frac{\partial}{\partial \mathbf{R}_{I}}\left[\varepsilon_{0}(\mathbf{R})+V_{n n}(\mathbf{R})\right]
$$






Hayes and MET
JACS 129, 12172 (2007)


## Hellman-Feynman Theorem

Ground-state electronic surface as expectation value:

$$
\begin{gathered}
\varepsilon_{0}(\mathbf{R})=\left\langle\varphi_{0}(\mathbf{R})\right| \hat{H}^{(e)}(\mathbf{R})\left|\varphi_{0}(\mathbf{R})\right\rangle \quad \hat{H}^{(e)}(\mathbf{R})=\hat{T}_{e}+V_{e e}(\hat{\mathbf{r}})+V_{e n}(\hat{\mathbf{r}}, \mathbf{R}) \\
\frac{\partial \varepsilon_{0}}{\partial \mathbf{R}_{I}}=\left\langle\varphi_{0}(\mathbf{R})\right| \frac{\partial \hat{H}^{(e)}}{\partial \mathbf{R}_{I}}\left|\varphi_{0}(\mathbf{R})\right\rangle+\left\langle\frac{\partial \varphi_{0}}{\partial \mathbf{R}_{I}}\right| \hat{H}^{(e)}(\mathbf{R})\left|\varphi_{0}(\mathbf{R})\right\rangle+\left\langle\varphi_{0}(\mathbf{R})\right| \hat{H}^{(e)}(\mathbf{R})\left|\frac{\partial \varphi_{0}}{\partial \mathbf{R}_{I}}\right\rangle \\
\frac{\partial \varepsilon_{0}}{\partial \mathbf{R}_{I}}=\left\langle\varphi_{0}(\mathbf{R})\right| \frac{\partial \hat{H}^{(e)}}{\partial \mathbf{R}_{I}}\left|\varphi_{0}(\mathbf{R})\right\rangle
\end{gathered}
$$

Because $\quad\left\langle\varphi_{0}(\mathbf{R}) \mid \varphi_{0}(\mathbf{R})\right\rangle=1$

$$
\frac{\partial}{\partial \mathbf{R}_{I}}\left\langle\varphi_{0}(\mathbf{R}) \mid \varphi_{0}(\mathbf{R})\right\rangle=0
$$

## Hartree-Fock and post Hartree-Fock methods

Antisymmetric product (Slater determinant) ansatz of single-particle orbitals for ground-state wave function:

$$
\varphi_{0}\left(\mathbf{x}_{1}, \ldots, \mathbf{x}_{M}\right)=\left|\begin{array}{ccc}
\psi_{1}\left(\mathbf{x}_{1}\right) & \cdots & \psi_{1}\left(\mathbf{x}_{M}\right) \\
\vdots & \ddots & \vdots \\
\psi_{M}\left(\mathbf{x}_{1}\right) & \cdots & \psi_{M}\left(\mathbf{x}_{M}\right)
\end{array}\right| \equiv \varphi_{\mathrm{HF}}, \quad\left\langle\psi_{i} \mid \psi_{j}\right\rangle=\delta_{i j}
$$

Variationally optimizing

$$
\left\langle\varphi_{0}\right| \hat{H}^{(\mathrm{e})}\left|\varphi_{0}\right\rangle=\left\langle\varphi_{\mathrm{HF}}\right| \hat{H}^{(\mathrm{e})}\left|\varphi_{\mathrm{HF}}\right\rangle
$$

with respect to the single-particle orbitals subject to the orthogonality condition, gives the Hartree-Fock equations:
$\left[-\frac{1}{2} \nabla^{2}+V_{e n}(\mathbf{r})+e^{2} \sum_{\ell} \int d \mathbf{x}^{\prime} \frac{\left|\psi_{\ell}\left(\mathbf{x}^{\prime}\right)\right|^{2}}{\left|\mathbf{r}-\mathbf{r}^{\prime}\right|}\right] \psi_{j}(\mathbf{x})-\sum_{\ell \in \mathrm{occ}} \int d \mathbf{x}^{\prime} \frac{\psi_{\ell}^{*}\left(\mathbf{x}^{\prime}\right) \psi_{j}\left(\mathbf{x}^{\prime}\right)}{\left|\mathbf{r}-\mathbf{r}^{\prime}\right|} \psi_{\ell}(\mathbf{x})=\tilde{\varepsilon}_{j} \psi_{j}(\mathbf{x})$
$\tilde{\varepsilon}_{i}$ are the eigenvalues of a Lagrange multiplier matrix for enforcing the orthogonality condition.

Configuration interaction:

$$
\begin{gathered}
\left|\varphi_{0}\right\rangle=c_{0}\left|\varphi_{\mathrm{HF}}\right\rangle+\sum_{r, a} c_{a}^{r}\left|\varphi_{a}^{r}\right\rangle+\sum_{a<b, r<s} c_{a b}^{r s}\left|\varphi_{a b}^{r s}\right\rangle+\sum_{a<b<c, r<s<t} c_{a b c}^{r s t}\left|\varphi_{a b c}^{r s t}\right\rangle+\cdots \\
N
\end{gathered}
$$

Example of excitations for $\mathrm{H}_{2}$ :



Single Excitation

$$
\sigma_{\mathrm{g}}^{1} \sigma_{\mathrm{u}}^{* 1}
$$



Double Excitation

$$
\sigma_{u}^{* 2}
$$

In principle exact, but scaling is $N$ ! to reach "exact" results, noting that if a single-particle basis set is used in each of the determinants, then the basis-set limit must be reached.

Coupled cluster theory: $\quad\left|\varphi_{0}\right\rangle=e^{\hat{T}}\left|\varphi_{\mathrm{HF}}\right\rangle$

$$
\begin{aligned}
& \left|\varphi_{0}\right\rangle=\left[1+\hat{T}+\frac{1}{2!} \hat{T}^{2}+\frac{1}{3!} \hat{T}^{3}+\cdots\right]\left|\varphi_{\mathrm{HF}}\right\rangle \\
& \hat{T}=\hat{T}_{1}+\hat{T}_{2}+\hat{T}_{3}+\cdots \quad \hat{T}_{1}\left|\varphi_{\mathrm{HF}}\right\rangle=\sum_{r, a} t_{a}^{r}\left|\varphi_{a}^{r}\right\rangle
\end{aligned}
$$

Full CC and full Cl are closely related. However, when the

$$
\hat{T}_{2}\left|\varphi_{\mathrm{HF}}\right\rangle=\sum_{a<b, r<s} t_{a b}^{r s}\left|\varphi_{a b}^{r s}\right\rangle
$$ CC expansion is truncated, as it usually is, then it is not strictly variational.

$$
\hat{T}_{3}\left|\varphi_{\mathrm{HF}}\right\rangle=\sum_{a<b<c, r<s<t} t_{a b c}^{r s t}\left|\varphi_{a b c}^{r s t}\right\rangle
$$

$$
\begin{aligned}
& \hat{H}^{(e)}\left|\varphi_{0}\right\rangle=\varepsilon_{0}\left|\varphi_{0}\right\rangle \\
& \hat{H}^{(e)} e^{\hat{T}}\left|\varphi_{\mathrm{HF}}\right\rangle=\varepsilon_{0} e^{\hat{T}}\left|\varphi_{\mathrm{HF}}\right\rangle \\
& e^{-\hat{T}} \hat{H}^{(e)} e^{\hat{T}}\left|\varphi_{\mathrm{HF}}\right\rangle=\varepsilon_{0}\left|\varphi_{\mathrm{HF}}\right\rangle
\end{aligned}
$$

$$
\begin{aligned}
& \left\langle\varphi_{H F}\right| e^{-\hat{T}} \hat{H}^{(e)} e^{\hat{T}}\left|\varphi_{\mathrm{HF}}\right\rangle=\varepsilon_{0} \\
& \left\langle\varphi_{a b c \ldots}^{\text {st... }}\right| e^{-\hat{T}} \hat{H}^{(e)} e^{\hat{T}}\left|\varphi_{\mathrm{HF}}\right\rangle=0
\end{aligned}
$$

## Hohenberg-Kohn Theorem

- Two systems with the same number $N_{\mathrm{e}}$ of electrons have the same $T_{e}+V_{e e}$. Hence, they are distinguished only by $V_{e n}$.
- Knowledge of $\left|\Psi_{0}\right\rangle$ determines $V_{e n}$.
- Let $\mathcal{V}$ be the set of external potentials such that solution of

$$
\hat{H}_{e} \Psi=\left[\hat{T}_{e}+\hat{V}_{e e}+\hat{V}_{e n}\right] \Psi_{0}=\varepsilon_{0} \Psi_{0}
$$

yields a non-degenerate ground state $\left|\Psi_{0}\right\rangle$.
Collect all such ground state wavefunctions into a set $\boldsymbol{\Psi}$. Each element of this set is associated with a Hamiltonian determined by the external potential.

There exists a 1:1 mapping $C$ such that


## Hohenberg-Kohn Theorem

Let $V_{e n}$ and $V_{e n}^{\prime}$ be two elements of $\mathcal{V}$ such that $V_{e n} \neq V_{e n}^{\prime}+$ const Let $\left|\Psi_{0}\right\rangle$ and $\left|\Psi_{0}^{\prime}\right\rangle$ be the associated ground-state wave functions

$$
\begin{align*}
& \left(\hat{T}_{e}+\hat{V}_{e e}+\hat{V}_{e n}\right)\left|\Psi_{0}\right\rangle=\varepsilon_{0}\left|\Psi_{0}\right\rangle  \tag{1}\\
& \left(\hat{T}_{e}+\hat{V}_{e e}+\hat{V}_{e n}^{\prime}\right)\left|\Psi_{0}^{\prime}\right\rangle=\varepsilon_{0}^{\prime}\left|\Psi_{0}^{\prime}\right\rangle \tag{2}
\end{align*}
$$

Assume $\left|\Psi_{0}\right\rangle=\left|\Psi_{0}^{\prime}\right\rangle$

$$
\left(\hat{T}_{e}+\hat{V}_{e e}+\hat{V}_{e n}^{\prime}\right)\left|\Psi_{0}\right\rangle=\varepsilon_{0}^{\prime}\left|\Psi_{0}\right\rangle
$$

Subtracting (1) from (2') the two yields

$$
\left(V_{e n}-V_{e n}^{\prime}\right)\left|\Psi_{0}\right\rangle=\left(\varepsilon_{0}-\varepsilon_{0}^{\prime}\right)\left|\Psi_{0}\right\rangle
$$

Implying that $V_{e n}-V_{e n}^{\prime}=\varepsilon_{0}-\varepsilon_{0}^{\prime}=$ const
Hence $\left|\Psi_{0}\right\rangle \neq\left|\Psi_{0}^{\prime}\right\rangle$ and $C$ exists, and similarly $C^{-1}$ exists.

## Hohenberg-Kohn Theorem

Inverse map:

$$
C^{-1} \quad: \quad \boldsymbol{\Psi} \rightarrow \mathcal{V}
$$

To prove: $\quad\left|\Psi_{0}\right\rangle \neq\left|\Psi_{0}^{\prime}\right\rangle \Rightarrow V_{e n} \neq V_{e n}^{\prime}$
Assume $V_{e n}=V_{e n}^{\prime}$, then

$$
\begin{aligned}
& \left(\hat{T}_{e}+\hat{V}_{e e}+\hat{V}_{e n}\right)\left|\Psi_{0}\right\rangle=\varepsilon_{0}\left|\Psi_{0}\right\rangle \\
& \left(\hat{T}_{e}+\hat{V}_{e e}+\hat{V}_{e n}\right)\left|\Psi_{0}^{\prime}\right\rangle=\varepsilon_{0}^{\prime}\left|\Psi_{0}^{\prime}\right\rangle
\end{aligned}
$$

These statements cannot both be true because the Hamiltonian is the same. Therefore, $V_{e n} \neq V_{e n}^{\prime}$ and $C^{-1}$ exists.

## Hohenberg-Kohn Theorem (part II)

Given an antisymmetric ground state wavefunction from the set $\boldsymbol{\Psi}$, the ground-state density is given by

$$
n_{0}(\mathbf{r})=N_{e} \sum_{s_{1}} \cdots \sum_{s_{N_{e}}} \int d \mathbf{r}_{2} \cdots d \mathbf{r}_{N_{e}}\left|\Psi_{0}\left(\mathbf{r}, s_{1}, \mathbf{x}_{2}, \ldots, \mathbf{x}_{N_{e}}\right)\right|^{2}
$$

Knowledge of $n_{0}(\mathbf{r})$ is sufficient to determine $\left|\Psi_{0}\right\rangle$
Let $\mathcal{N}$ be the set of ground state densities obtained from $N_{e}$-electron ground state wavefunctions in $\boldsymbol{\Psi}$. Then, there exists a 1:1 mapping


$$
D^{-1}: \mathcal{N} \longrightarrow \boldsymbol{\Psi}
$$

The formula for $n(\mathbf{r})$ shows that $D$ exists, however, showing that $D^{-1}$ exists Is less trivial.

## Hohenberg-Kohn Theorem (part II)

By variational principle

$$
\varepsilon_{0}=\left\langle\Psi_{0}\right| \hat{H}_{e}\left|\Psi_{0}\right\rangle<\left\langle\Psi_{0}^{\prime}\right| \hat{H}_{e}\left|\Psi_{0}^{\prime}\right\rangle
$$

Note

$$
\begin{aligned}
\left\langle\Psi_{0}^{\prime}\right| \hat{H}_{e}\left|\Psi_{0}^{\prime}\right\rangle & =\left\langle\Psi_{0}^{\prime}\right| \hat{H}_{e}^{\prime}+\hat{V}_{e n}-\hat{V}_{e n}^{\prime}\left|\Psi_{0}^{\prime}\right\rangle \\
& =\varepsilon_{0}^{\prime}+\left\langle\Psi_{0}^{\prime}\right| \hat{V}_{e n}-\hat{V}_{e n}^{\prime}\left|\Psi_{0}^{\prime}\right\rangle \\
& =\varepsilon_{0}^{\prime}+\int d \mathbf{r}\left[V_{e n}(\mathbf{r})-V_{e n}^{\prime}(\mathbf{r})\right] n_{0}^{\prime}(\mathbf{r})
\end{aligned}
$$

Hence,

$$
\varepsilon_{0}<\varepsilon_{0}^{\prime}+\int d \mathbf{r}\left[V_{e n}(\mathbf{r})-V_{e n}^{\prime}(\mathbf{r})\right] n_{0}^{\prime}(\mathbf{r})
$$

Similarly,

$$
\varepsilon_{0}^{\prime}=\left\langle\Psi_{0}^{\prime}\right| \hat{H}_{e}^{\prime}\left|\Psi_{0}^{\prime}\right\rangle<\left\langle\Psi_{0}\right| \hat{H}_{e}^{\prime}\left|\Psi_{0}^{\prime}\right\rangle=\varepsilon_{0}-\int d_{\mathbf{r}}\left[V_{e n}\left(\mathbf{Y}^{\infty}\right)-V_{e n}^{\prime}\left(\mathbf{Y}^{\infty}\right)\right] \boldsymbol{M}_{0}\left(\mathbf{r}^{\infty}\right)
$$

Note:

$$
n_{0}^{\prime}(r)=n_{0}(r) \quad \Rightarrow \varepsilon_{0}+\varepsilon_{0}^{\prime}<\varepsilon_{0}^{\prime}+\varepsilon_{0}
$$

Therefore, $n_{0}(\mathbf{r}) \neq n_{0}^{\prime}(\mathbf{r})$ and $D^{-1}$ exists

## Hohenberg-Kohn Theorem

Since $C^{-1}$ and $D^{-1}$ exist, we compose them to give the map

$$
(C D)^{-1}: \mathcal{N} \rightarrow \mathcal{V}
$$

- Knowledge of $n_{0}(r)$ uniquely determines $\hat{H}_{e}$
- Knowledge of $n_{0}(r)$ uniquely determines ground state properties

Given an operator $\hat{O}$, the ground-state expectation value

$$
\langle\hat{O}\rangle=\left\langle\Psi_{0}\left[n_{0}\right]\right| \hat{O}\left|\Psi_{0}\left[n_{0}\right]\right\rangle=O\left[n_{0}\right]
$$

is a unique functional of $n_{0}(\mathbf{r})$

## Energy functional

$$
\left\langle\hat{H}_{e}\right\rangle=\left\langle\Psi_{0}\left[n_{0}\right]\right| \hat{H}_{e}\left|\Psi_{0}\left[n_{0}\right]\right\rangle=E\left[n_{0}\right]=\varepsilon_{0}
$$

By the variational principle, for some $|\Psi[n]\rangle$ in $\boldsymbol{\Psi}$

$$
E[n]=\langle\Psi[n]| \hat{H}_{e}|\Psi[n]\rangle \geq\left\langle\Psi_{0}\left[n_{0}\right]\right| \hat{H}_{e}\left|\Psi_{0}\left[n_{0}\right]\right\rangle=E\left[n_{0}\right]
$$

Minimization principle

$$
\varepsilon_{0}=E\left[n_{0}\right]=\min _{n(\mathbf{r}) \in \mathcal{N}} E[n]
$$

$v$-representability: A density $n(\mathbf{r})$ is $v$-representable if it is associated with the ground-state wave function of some Hamiltonian $\hat{H}_{e}$
$N$-representability: A density $n(\mathbf{r})$ is $N$-representable if it is associated with an antisymmetric wave function, not necessarily associated with a Hamiltonian $\hat{H}_{e}$

$$
n(\mathbf{r}) \geq 0, \quad \int d \mathbf{r} n(\mathbf{r})=N_{e}
$$

Hohenberg-Kohn theorem only pertains to $v$-representable densities.

## Hohenberg-Kohn functional and the Levy procedure

Let $\left|\Psi_{n_{0}}\right\rangle$ be an antisymmetric wave function that gives $n_{0}(\mathbf{r})$
$\left\langle\Psi_{n_{0}}\right| \hat{T}_{e}+\hat{V}_{e e}\left|\Psi_{n_{0}}\right\rangle+\int d \mathbf{r} n_{0}(\mathbf{r}) V_{e n}(\mathbf{r}) \geq\left\langle\Psi_{0}\right| \hat{T}_{e}+\hat{V}_{e e}\left|\Psi_{0}\right\rangle+\int d \mathbf{r} n_{0}(\mathbf{r}) V_{e n}(\mathbf{r})$
$F[n]$ is called the Hohenberg-Kohn functional, which is universal.

$$
F\left[n_{0}\right]=\min _{\left|\Psi_{n_{0}}\right| \rightarrow n_{0}(\mathbf{r})}\left\langle\Psi_{n_{0}}\right| \hat{T}_{e}+\hat{V}_{e e}\left|\Psi_{n_{0}}\right\rangle
$$

Define:

$$
\tilde{F}[n]=\min _{|\Psi\rangle \rightarrow n(\mathbf{r})}\langle\Psi| \hat{T}_{e}+\hat{V}_{e e}|\Psi\rangle
$$

Since $\tilde{F}\left[n_{0}\right]=F\left[n_{0}\right]$, we reformulate the minimization as

$$
\begin{aligned}
\mathcal{E}_{0} & =\min _{n(\mathbf{r})}\left[\min _{|\Psi\rangle \rightarrow n(\mathbf{r})}\langle\Psi| \hat{T}_{e}+\hat{V}_{e e}|\Psi\rangle+\int d \mathbf{r} n(\mathbf{r}) V_{e n}(\mathbf{r})\right] \\
& =\min _{n(\mathbf{r})}\left[\tilde{F}[n]+\int d \mathbf{r} n(\mathbf{r}) V_{e n}(\mathbf{r})\right]
\end{aligned}
$$

which requires that $n(\mathbf{r})$ only be $N$-representable.

## Kohn-Sham density functional theory

The kinetic energy and exchange-correlation functionals are unknown. In KS theory, we map our fully interacting system onto an equivalent non-interacting system (albeit with a complicated potential) and introduce single-particle orbitals.

Wave function ansatz:

$$
\varphi_{0}\left(\mathbf{x}_{1}, \ldots, \mathbf{x}_{M}\right)=\left|\begin{array}{ccc}
\psi_{1}\left(\mathbf{x}_{1}\right) & \cdots & \psi_{1}\left(\mathbf{x}_{M}\right) \\
\vdots & \ddots & \vdots \\
\psi_{M}\left(\mathbf{x}_{1}\right) & \cdots & \psi_{M}\left(\mathbf{x}_{M}\right)
\end{array}\right|
$$

Single-particle orbitals: $\quad \psi_{i}(\mathbf{x}) \quad\left\langle\psi_{i} \mid \psi_{j}\right\rangle=\delta_{i j}$

Electron density:

$$
n(\mathbf{r})=M \sum_{s_{1}} \cdots \sum_{s_{M}} \int d \mathbf{r}_{2} \cdots d \mathbf{r}_{M}\left|\varphi_{0}\left(\mathbf{x}_{1}, \ldots, \mathbf{x}_{M}\right)\right|^{2}=\sum_{i=1}^{M} \sum_{s_{z}=-1 / 2}^{1 / 2}\left|\psi_{i}(\mathbf{x})\right|^{2}
$$

## Kohn-Sham density functional theory

Now, at least the kinetic energy is known. The total energy functional of KS theory is:

$$
E[\{\psi\}, \mathbf{R}]=T_{s}[\{\psi\}]+E_{H}[n]+E_{x c}[n]+E_{e n}[n, \mathbf{R}]
$$

Energy definitions:

$$
\begin{gathered}
T_{s}[\{\psi\}]=-\frac{1}{2} \sum_{i}\left\langle\psi_{i}\right| \nabla^{2}\left|\psi_{i}\right\rangle \quad E_{H}[n]=\frac{1}{2} \int d \mathbf{r} d \mathbf{r}^{\prime} \frac{n(\mathbf{r}) n\left(\mathbf{r}^{\prime}\right)}{\left|\mathbf{r}-\mathbf{r}^{\prime}\right|} \\
E_{e n}[n, \mathbf{R}]=-\sum_{I} Z_{I} \int d \mathbf{r} \frac{n(\mathbf{r})}{\left|\mathbf{r}-\mathbf{R}_{I}\right|}
\end{gathered}
$$

Ground-state energy via constrained minimization

$$
\varepsilon_{0}(\mathbf{R})=\min _{\{\psi\}}\left[E[\{\psi\}, \mathbf{R}]-\sum_{i, j} \lambda_{i j}\left(\left\langle\psi_{i} \mid \psi_{j}\right\rangle-\delta_{i j}\right)\right]
$$

Kohn-Sham equations ( $\varepsilon_{i}$ are eigenvalues of $\lambda_{i j}$ )

$$
\left[-\frac{1}{2} \nabla^{2}+V_{K S}(\mathbf{r})\right] \psi_{i}(\mathbf{r})=\varepsilon_{i} \psi_{i}(\mathbf{r}) \quad V_{K S}(\mathbf{r})=\frac{\delta}{\delta n(\mathbf{r})}\left(E_{H}+E_{x c}+E_{e n}\right)
$$

## Approximating exchange and correlation

Local density approximation for exchange: Consider an ideal electron gas in a periodic cubic box of side $L$ and volume $V=L^{3}$. The single particle eigenfunctions and energies are

$$
\psi_{\mathbf{n} m}(\mathbf{x})=\frac{1}{\sqrt{V}} e^{2 \pi \mathrm{in} \cdot \mathbf{r} / L} \sigma_{m}\left(s_{z}\right), \quad \varepsilon_{\mathbf{n}}=\frac{2 \pi^{2}}{L^{2}}|\mathbf{n}|^{2}
$$

Exchange energy:

$$
E_{x}=-\frac{1}{4} \int d \mathbf{r} d \mathbf{r}^{\prime} \frac{\left|\rho_{1}\left(\mathbf{r}, \mathbf{r}^{\prime}\right)\right|^{2}}{\left|\mathbf{r}-\mathbf{r}^{\prime}\right|}
$$

Single-particle density matrix:

$$
\rho_{1}\left(\mathbf{r}, \mathbf{r}^{\prime}\right)=\sum_{S_{z}, S_{z}^{\prime}} \sum_{m} \sum_{\mathbf{n}} \psi_{\mathbf{n} m}(\mathbf{x}) \psi_{\mathbf{n} m}^{*}\left(\mathbf{x}^{\prime}\right) \theta\left(\varepsilon_{F}-\varepsilon_{\mathbf{n}}\right)
$$

Evaluate in the thermodynamic limit:

$$
E_{x}=-\frac{3}{4}\left(\frac{3}{\pi}\right)^{1 / 3} V n^{4 / 3}=C_{x} V n^{4 / 3}
$$

As a functional of spatially varying density $n(\mathbf{r})$

$$
E_{x}[n]=C_{x} \int d \mathbf{r} n^{4 / 3}(\mathbf{r})
$$

## Approximating exchange and correlation

Generalized gradient approximation:

$$
E_{x c}[n]=\int d \mathbf{r} f(n(\mathbf{r}), \nabla n(\mathbf{r}))
$$

Becke exchange (1988):

$$
E_{x}[n]=E_{x}^{\mathrm{LDA}}[n]-\beta \int d \mathbf{r} n^{4 / 3}(\mathbf{r}) \frac{x^{2}}{1+6 \beta x \sinh ^{-1} x}, \quad x=\frac{|\nabla n(\mathbf{r})|}{n^{4 / 3}(\mathbf{r})}
$$

Asymptotic behavior:

$$
n(r) \sim e^{-a r} \quad \Rightarrow \quad E_{x} \sim-\frac{1}{r}
$$

General strategies:

- Fit parameters to thermochemical properties of particular sets of molecules.
- Determine based on known properties of exchange $E_{\mathrm{xc}}$ functional, e.g., PW91, PBE, ...


## Radial distribution functions for BLYP Water


H. -S. Lee and MET, JPCA 110, 549 (2006)
H. -S. Lee and MET JCP 125, 154507 (2006).
H. -S. Lee and MET JCP 126, 164501 (2007).
Z. Ma and MET JCP 137, 044506 (2012).

Neutron: Soper, et. al. JCP 106, 247 (1997)
X-ray: Hura, et. al. Chem. Phys. 113, 9140 (2000)

Grid $=75^{3}, \quad t=60 \mathrm{ps}$
Ensemble: NVT, $300 \mathrm{~K}, \mu=500$ au


Exp. Data from A. K. Soper
J. Phys. Condens. Matter 19, 3352 (2007)

Theor. Data from Lee and Tuckerman
J. Chem. Phys. 125, 154507 (2006).

Functional = BLYP
Converged DVR basis set
NPT calculations give a density of $0.92 \mathrm{~g} / \mathrm{cm}^{3}$
Z. Ma, Y. Zhang, MET JCP (2012).

From Medders et al. JCTC (2014)


## Approximating exchange and correlation

Meta-generalized gradient approximation:

$$
E_{x c}[n, \tau]=\int d \mathbf{r} f\left(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^{2} n(\mathbf{r}), \tau(\mathbf{r})\right)
$$

where the kinetic energy density is $\quad \tau(\mathbf{r})=\sum_{i=1}^{M} \sum_{s_{z}=-1 / 2}^{1 / 2}\left|\nabla \psi_{i}(\mathbf{x})\right|^{2}$

Example: SCAN functional of Perdew and coworkers:
Nature Chem. 8, 831 (2016).


## Approximating exchange and correlation

Hybrid functionals:

$$
\begin{aligned}
& E_{x c}[n,\{\psi\}]=\alpha E_{x}^{\mathrm{HF}}[\{\psi\}]+(1-\alpha) E_{x}^{\mathrm{DFT}}[n]+E_{c}^{\mathrm{DFT}}[n] \\
& E_{x}^{H F}=-\frac{1}{4} \sum_{j, \ell \in \mathrm{coc}} \int d \mathbf{x} d \mathbf{x}^{\prime} \frac{\psi_{\ell}(\mathbf{x}) \psi_{\ell}^{*}\left(\mathbf{x}^{\prime}\right) \psi_{j}\left(\mathbf{x}^{\prime}\right) \psi_{j}^{*}(\mathbf{x})}{\left|\mathbf{r}-\mathbf{r}^{\prime}\right|}
\end{aligned}
$$

Most well known examples include B3LYP, PBE0, HSE (range-separated), M-yy family.
Including partial exact correlation (within RPA) [see e.g. Ren et al. J. Mat.Sci. (2012), which also discusses the connection to coupled cluster theory]:

$$
\begin{gathered}
E_{c}^{\mathrm{RPA}}=\frac{1}{2 \pi} \int_{0}^{\infty} d \omega \int d \mathbf{x} d \mathbf{x}^{\prime}\left[\ln \left(1-\frac{\chi^{0}\left(\mathbf{x}, \mathbf{x}^{\prime} ; i \omega\right)}{\left|\mathbf{r}-\mathbf{r}^{\prime}\right|}\right)+\frac{\chi^{0}\left(\mathbf{x}, \mathbf{x}^{\prime} ; i \omega\right)}{\left|\mathbf{r}-\mathbf{r}^{\prime}\right|}\right] \\
\chi^{0}\left(x, x^{\prime} ; i \omega\right)=\sum_{j, l} \frac{\left(f_{j}-f_{l}\right) \psi_{\ell}(\mathbf{x}) \psi_{\ell}^{*}\left(\mathbf{x}^{\prime}\right) \psi_{j}\left(\mathbf{x}^{\prime}\right) \psi_{j}^{* *}(\mathbf{x})}{\tilde{\varepsilon}_{j}-\tilde{\varepsilon}_{l}-i \omega}
\end{gathered}
$$

## Approximating DFT: Jacob's Ladder



Hartree World

## Including dispersion interactions

Weak dispersion forces are poorly described within the majority of DFT approximations.
Several techniques exist for including dispersion:

1. As an empirical a posteriori correction:

$$
E_{e n}[n, \mathbf{R}]=\int d \mathbf{r} n(\mathbf{r}) v_{e n}(\mathbf{r}, \mathbf{R})+U_{\mathrm{disp}}(\mathbf{R})
$$

e.g., Grimme's D2, Grimme's D3,....
2. As an a posteriori self-consistent correction:

$$
E_{e n}[n, \mathbf{R}]=\int d \mathbf{r} n(\mathbf{r}) v_{e n}(\mathbf{r}, \mathbf{R})+U_{\mathrm{disp}}[n, \mathbf{R}]
$$

e.g., Tkatchenko-Scheffler [Phys. Rev. Lett. 102, 073005 (2009)].
3. Inclusion via additional 1-electron potential in $v_{\mathrm{en}}(\mathbf{r}, \mathbf{R})$, e.g., the DCACP method [von Lilienfeld et al. Phys. Rev. Lett. 93, 153004 (2004)].
4. Build into $E_{\mathrm{xc}}[n]$, e.g., Dion et al. Phys.Rev.Lett. 92, 246401 (2004) and implementation by Soler et al. Phys. Rev. Lett. 103095102 (2009).


From Marsalek and Markland J. Phys. Chem. Lett. 8, 1545 (2017).



## Predicted crystal structures



| Polymorph | Coumarin $\mathbf{I}^{8}$ | Coumarin $\mathbf{I I}^{\text {a }}$ | Coumarin III $^{\text {a }}$ | Coumarin $\mathbf{I V}^{\text {a }}$ | Coumarin $\mathbf{V}^{\text {b }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Space group | Pca ${ }_{1}$ | $P 2{ }_{1}$ | $P 2{ }_{2}{ }_{1}{ }_{1}$ | $P 22_{1} 2_{1}$ | $P 22_{12} 2_{1}$ |
| $a(\AA)$ | 15.5023(11) | 3.980 | 17.066 | 24.722 | 4.868 |
| $b$ ( $\AA$ ) | 5.6630(4) | 15.291 | 6.038 | 5.994 | 6.882 |
| $c(\AA)$ | 7.9102(6) | 5.858 | 13.888 | 14.310 | 20.851 |
| $\beta\left({ }^{\circ}\right)$ | 90 | 85.76 | 90 | 90 | 90 |
| $V\left(\AA^{3}\right)$ | 694.4 | 355.5 | 1431.0 | 2120.5 | 698.4 |
| $Z, Z^{\prime}$ | 4, 1 | 2, 1 | 8, 2 | 12, 3 | 4, 1 |



## Performance of different DFT functionals in ranking the polymorphs



## Periodic boundary conditions and Bloch's Theorem

If we impose periodic bondary conditions on the system, then we impose periodicity on the potential appearing in the Schrödinger equation.


Let $\mathbf{S}=(n, l, m) L$, then

$$
V(\mathbf{r})=V(\mathbf{r}+\mathbf{S})
$$

Schrödinger equation:

$$
H(\mathbf{r}) \psi(\mathbf{r})=\left[-\frac{1}{2} \nabla^{2}+V(\mathbf{r})\right] \psi(\mathbf{r})=\varepsilon \psi(\mathbf{r})
$$

## Periodic boundary conditions and Bloch's Theorem

Define a lattice translation operator $T_{\mathrm{S}}$ by

$$
T_{\mathbf{S}} \psi(\mathbf{r})=\psi(\mathbf{r}+\mathbf{S})
$$

Because $V$ is periodic, so is the Hamiltonian: $H(\mathbf{r}+\mathbf{S})=H(\mathbf{r})$
Consequently,

$$
\begin{aligned}
& {\left[H(\mathbf{r}), T_{\mathrm{s}}\right] \psi(\mathbf{r})=\left(H(\mathbf{r}) T_{\mathrm{S}}-T_{\mathbf{s}} H(\mathbf{r})\right) \psi(\mathbf{r})} \\
& =H(\mathbf{r}) \psi(\mathbf{r}+\mathbf{S})-H(\mathbf{r}+\mathbf{S}) T_{\mathbf{S}} \psi(\mathbf{r}) \\
& =H(\mathbf{r}) \psi(\mathbf{r}+\mathbf{S})-H(\mathbf{r}) \psi(\mathbf{r}+\mathbf{S}) \\
& =0 \\
& {\left[H(\mathbf{r}), T_{\mathrm{s}}\right]=0}
\end{aligned}
$$

Therefore, $\psi(\mathrm{r})$ is also an eigenstate of $T_{\mathbf{S}}$

$$
\begin{aligned}
& H \psi(\mathbf{r})=\varepsilon \psi(\mathbf{r}) \\
& T_{\mathbf{s}} \psi(\mathbf{r})=\lambda(\mathbf{S}) \psi(\mathbf{r})
\end{aligned}
$$

## Periodic boundary conditions and Bloch's theorem

Now

$$
T_{\mathrm{S}} T_{\mathbf{S}^{\prime}}=T_{\mathbf{S}^{\prime}} T_{\mathrm{S}}=T_{\mathbf{S}+\mathbf{S}^{\prime}}
$$

which means

$$
\lambda(\mathbf{S}) \lambda\left(\mathbf{S}^{\prime}\right)=\lambda\left(\mathbf{S}+\mathbf{S}^{\prime}\right)
$$

We will show that $\lambda(\mathbf{S})$ must be of the form

$$
\lambda(\mathbf{S})=e^{i \mathbf{k} \cdot \mathbf{S}}
$$

where

$$
\mathbf{k}=x_{1} \mathbf{g}_{1}+x_{2} \mathbf{g}_{2}+x_{3} \mathbf{g}_{3}
$$

The reciprocal lattice vectors satisfy

$$
\mathbf{g}_{i} \bullet \mathbf{a}_{j}=2 \pi \delta_{i j}
$$

## Periodic boundary conditions and Bloch's theorem

Take as an ansatz

$$
\psi(\mathbf{r})=e^{i \mathbf{k} \cdot \mathbf{r}} u(\mathbf{r})
$$

where $u(\mathbf{r})$ is a strictly periodic function.

$$
\begin{aligned}
& u(\mathbf{r})= e^{-i \mathbf{k} \cdot \mathbf{r}} \psi(\mathbf{r}) \\
& \begin{aligned}
u(\mathbf{r}+\mathbf{S}) & =e^{-i \mathbf{k} \cdot(\mathbf{r}+\mathbf{S})} \psi(\mathbf{r}+\mathbf{S}) \\
& =e^{-i \mathbf{k} \cdot \mathbf{r}} e^{-i \mathbf{k} \cdot \mathbf{S}} T_{S} \psi(\mathbf{r}) \\
& =e^{-i \mathbf{k} \cdot \mathbf{r}} e^{-i \mathbf{k} \cdot \mathbf{S}} e^{i \mathbf{k} \cdot \mathbf{S}} \psi(\mathbf{r}) \\
& =e^{-i \mathbf{k} \cdot \mathbf{r}} \psi(\mathbf{r}) \\
& =u(\mathbf{r})
\end{aligned}
\end{aligned}
$$

which justifies our ansatz.

