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Modeling Materials Properties and Functions: The Many-Body Schrödinger Equation

$$(\hat{T}^{e} + \hat{T}^{ion} + \hat{V}^{e-e} + \hat{V}^{e-ion} + \hat{V}^{ion-ion})\Psi = E\Psi$$
With: $\Psi(\mathbf{r}_{\mathbf{I}}, \dots \mathbf{r}_{\mathbf{N}}; \mathbf{R}_{\mathbf{I}}, \dots \mathbf{R}_{\mathbf{M}})$
 $\hat{T}^{e} = \sum_{k=1}^{N} \frac{\mathbf{p}_{k}^{2}}{2m}$
 $\hat{T}^{ion} = \sum_{I=1}^{M} \frac{\mathbf{P}_{I}^{2}}{2M_{I}}$
 $\hat{V}^{e-e} = \frac{1}{2} \frac{1}{4\pi\epsilon_{0}} \sum_{k\neq k'}^{N,N} \frac{e^{2}}{|\mathbf{r}_{\mathbf{k}} - \mathbf{r}_{\mathbf{k}'}|}$
 $\hat{V}^{ion-ion} = \frac{1}{2} \frac{1}{4\pi\epsilon_{0}} \sum_{l\neq l'}^{M,M} \frac{Z_{I}Z_{l'}}{|\mathbf{R}_{\mathbf{I}} - \mathbf{R}_{\mathbf{I}'}|}$
 $\hat{V}^{e-ion}(\mathbf{r}_{\mathbf{k}}, \mathbf{R}_{\mathbf{I}}) = \sum_{\mathbf{k}=1}^{N} \sum_{\mathbf{I}=1}^{M} \mathbf{v}_{\mathbf{I}}^{ion}(|\mathbf{R}_{\mathbf{I}} - \mathbf{r}_{\mathbf{k}}|)$
We know the operators and the interactions. We can write them down.
No open questions here!

Born-Oppenheimer Approximation

$$\Psi(\mathbf{r_1},\cdots,\mathbf{r_N};\mathbf{R_1},\cdots,\mathbf{R_M}) = \sum_{\nu} \Lambda_{\nu}(\{\mathbf{R_I}\}) \Phi_{\nu}\{\mathbf{R_I}\}(\{\mathbf{r_k}\})$$

Where Φ_v are solutions of the "electronic Hamiltonian":

 $H^{e}_{\{\mathbf{R}_{\mathbf{I}}\}}\Phi_{\nu,\{\mathbf{R}_{\mathbf{I}}\}}(\{\mathbf{r}_{\mathbf{k}}\}) = E^{e}_{\nu,\{\mathbf{R}_{\mathbf{I}}\}}\Phi_{\nu,\{\mathbf{R}_{\mathbf{I}}\}}(\{\mathbf{r}_{\mathbf{k}}\})$ $H^{e} = T^{e} + V^{e-e} + V^{e-ion}$

The Schrödinger equation of the electrons is determined by $\{\mathbf{R}_{I}, Z_{I}\}_{I=1}^{M}, N$

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frequently (commonly) applied approximations:

- neglect non-adiabatic coupling (terms of order m/M_I)
- keep only Λ_0

→ the dynamics of electrons and nuclei decouple

Some Limits of the Born-Oppenheimer Approximation

The BO Approximation does not account for correlated dynamics of ions and electrons. For example:

- polaron-induced superconductivity
- dynamical Jahn-Teller effect at defects in crystals
- some phenomena of diffusion in solids
- non-adiabaticity in molecule-surface scattering and chemical reactions
- relaxation and transport of charge carriers (e⁻ or h)
- etc.

Some Limits of the Born-Oppenheimer Approximation

The BO Approximation does not account for correlated dynamics of ions and electrons. For example:

polaron-induced superconductivity. These limits can be severe. Nevertheless, we will use the BO approximation in the following.
non-adia
relaxatio
etc.
H^e_{{**R**_{I}}} Φ_{ν,{**R**_{I}}}(**r**_{**k**}) = E^e_{v,{**R**_{I}}} Φ_{v,{**R**_{I}}}(**r**_{**k**}) H^e = T^e + V^{e-e} + V^{e-ion}



The Schrödinger equation of the electrons is determined by $\{\mathbf{R}_{l}, Z_{l}\}_{l=1}^{M}, N$ Given the ground-state electron density, *n*(*r*)

Inspection of $n(\mathbf{r})$ tells

- The positions of the atoms: {**R**_{*I*}}
- The nuclear charges at these positions: {Z_I}
- The total number of electrons: N

There is an obvious algorithm:

Ground-state density $n(\mathbf{r}) \rightarrow [\{\mathbf{R}_{I}, Z_{I}\}_{I=1}^{M}, N] \rightarrow \text{many-electron Schrödinger}$ equations \rightarrow ground-state energy (and even everything)

This is an algorithm, not a closed mathematical expression.

The Levy¹-Lieb² Constrained Search

With the external potential $v(\mathbf{r})$ (here the electron-nucleus Coulomb potential) and the concavity and continuity of the *ground-state energy* as a functional of $v(\mathbf{r})$ we have

$$E_0[v] = \operatorname{Min}_{n(\mathbf{r})} \left[\operatorname{Min}_{\Phi \to n(\mathbf{r})} < \Phi | T^e + V^{e-e} | \Phi > + \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \right] .$$

M. Levy, Proc. Natl. Acad. Sci. U.S.A. 76, 6062 (1979); M. Levy, Phys. Rev. A 26, 1200 (1982)
 E. Lieb, Int. Jour. Quant. Chem. 24, 243 (1983)

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Here $\Phi(\mathbf{r}_1, \mathbf{r}_2, ... \mathbf{r}_N)$ is an antisymmetric wavefunction of an *N*-electron system restricted to the request that it leads to $n(\mathbf{r})$.

This defines the *universal density functional* $F[n(\mathbf{r})]$ of the Hohenberg-Kohn DFT:

 $F[n] = \operatorname{Min}_{\Phi \to n(\mathbf{r})} < \Phi | T^e + V^{e-e} | \Phi > .$

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Kohn and Sham (1965):

$$E_v[n] = T_s[n] + \int v(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + E^{\text{Hartree}}[n] + E^{\text{xc}}[n]$$

with

$$E^{\text{Hartree}}[n] = \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}'$$

And $T_s[n]$ the functional of the kinetic energy of **noninteracting** electrons. $E^{xc}[n]$ contains all the unknowns.

Kohn and Sham (1965): $v^{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \frac{e^2}{4\pi\varepsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + \frac{\delta E^{\text{xc}}[n]}{\delta n(\mathbf{r})}$ Because $T_s[n]$ is the functional of non-interacting particles, we effectively restrict the allowed densities to those that can be written as $n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$

The xc Functional

 T_s , E^{Hartree} , and E^{xc} are all *universal* functionals in $n(\mathbf{r})$, i.e., they are independent of the special system studied. (general theory: see the work by Levy and Lieb)

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NOMAD Valence-Ele	ectron Density of Semiconductors
NOVEL MATERIALS DISCOVERY	a) Ge (top), b) GaAs (middle), and c) ZnSe (lower) in electrons per unit-cell volume.
	1 1 HAVE 1 1 HAVE 1 HAVE
	4 K Ca Sc Ti V Cr Ma Fe Co Ni Cu Za Ga Ge As Sc Br Kr 7 File N File N No File No No </th

V. L. Moruzzi, J. F. Janak, and A. R. Williams Calculated Electronic Properties of Metals Pergamon Press (1978)

NOVEL MATERIALS DISCOVERY

Approximations: LDA, 'muffin-tin' approximation, neglect of relativistic effects.

Quantitative data and trends:

Lattice constant, cohesive energy, bulk modulus, density of states, band structure, susceptibility enhancement, spin polarization.

Summary and Outlook: Interacting Electrons Determine the Properties and Function of Real Materials

NOVEL MATERIALS DISCOVERY

John Perdew: Correlated wavefunction theory provides "the right answer for the right reason", but at a high computational price for systems of many electrons. Kohn-Sham density-functional theory employs a simpler non-interacting or Coulomb-uncorrelated wavefunction, but includes a density functional for the exchangecorrelation (xc) energy that is exact in principle but requires improvable approximations in practice. It often provides "almost the right answer for almost the right reason at almost the right price" for real atoms, molecules, and materials.

Summary and Outlook: Interacting Electrons Determine the Properties and Function of Real Materials

NOVEL MATERIALS DISCOVERY

Important arenas for future theoretical work:

- Non-adiabatic effects, dissipation
- Transport (electrons, ions, heat)
- Thermodynamic phase transitions, e.g. melting
- Modeling the kinetics, e.g. of catalysts or crystal growth (self-assembly and self-organization) – in realistic environments
- Molecules and clusters (incl. bio molecules) in solvents, electrochemistry, fuel cells, external fields
- Correlated systems, e.g. *f*-electron chemistry
- Big-data analytics (statistical learning, compressed sensing, etc.)

The challenges:

- Find ways to control the xc approximation
- Develop methods for bridging length and time scales