The planewave pseudopotential method

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- Most low energy physics, chemistry and biology can be explained by the Quantum Mechanics of electrons and ions.
- In nearly all cases, treating the electrons as quantum mechanical alone is enough.

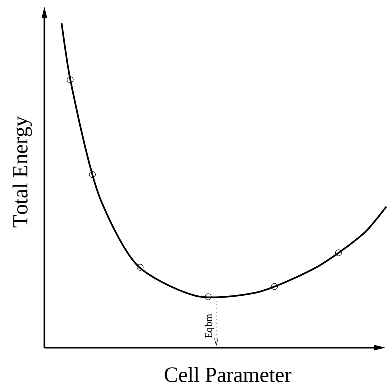
OVERVIEW

- Lecture I: The basic ingredients
  - Why total energy calculations?
  - DFT and the Kohn-Sham equations
  - Periodic boundary conditions and super-cells
  - Plane waves as a basis set
  - Pseudopotentials
  - How good is it?
- Lecture II: Tricks of the trade
  - Finding the groundstate
  - Forces and stresses
  - Geometry optimisation
  - Molecular dynamics
  - Application: Structural properties of lanthanides and actinides
  - The CASTEP code

- Lecture III: Analysis of results
  - Population analysis
  - Spectroscopies
  - Application: theoretical strength and cleavage of diamond
- Lecture IV: Applications
  - Core level and optical spectroscopies
  - Systematic prediction of crystal structures

Total Energy Calculations

- Many properties depend on the total energy of a system
  - equilibrium lattice constants (density)
  - bulk moduli
  - phonons
  - elastic constants
  - phase transitions
  - chemistry, bonding etc.



The Quantum Nightmare

- Solve -

$$
\begin{aligned}
H\Psi &= \sum_{i=1}^{N} (\frac{-\hbar^2}{2m}\nabla_i^2\Psi \\
&- Ze^2\sum_{\mathbf{R}}\frac{1}{|\mathbf{r_i}-\mathbf{R}|}\Psi) \\
&+ \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r_i}-\mathbf{r_j}|}\Psi \\
&= E\Psi,
\end{aligned}
$$

where Ψ is the manybody wavefunction

- The red term describes correlation
  - origin well known
  - very difficult to account for
  - still an area of active research for physicists (using e.g. QMC and GW techniques)

Density functional theory

- Hohenberg and Kohn proved that -

  "the total energy of an electron gas (even in the presence of a static external potential) is a unique function of the electron density, the minimum value of the functional is the ground state energy and the corresponding density yields the exact single particle ground-state density".

- gives hope of dealing with exchange and correlation
- but the functional is not known $\rightarrow$ Kohn-Sham
- a functional is a function of a function

$$E[n(\mathbf{r})] = T[n(\mathbf{r})] + E_{\mathrm{Ext}}[n(\mathbf{r})] + E_{\mathrm{H}}[n(\mathbf{r})] + E_{\mathrm{XC}}[n(\mathbf{r})]$$

The Kohn-Sham equations

$$
\begin{aligned}
E[\{\psi_i\}] &= 2\sum_i\int\psi_i[\frac{-\hbar^2}{2m}]\nabla^2\psi_i\mathbf{d^3r} \\
&+ \int V_{ion}(\mathbf{r})n(\mathbf{r})\mathbf{d^3r} \\
&+ \frac{e^2}{2}\int\frac{n(\mathbf{r})n(\mathbf{r'})}{|\mathbf{r}-\mathbf{r'}|})\mathbf{d^3rd^3r'} \\
&+ E_{XC}[n(\mathbf{r})] + E_{ion}(\mathbf{R_i})
\end{aligned}
$$

$$n(\mathbf{r}) = 2\sum_i|\psi_i(\mathbf{r})|^2$$

$$[\frac{-\hbar^2}{2m}]\nabla^2 + V_{ion}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r})]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})}\ldots$$

Exchange and Correlation Functionals

- We don't know $E_{XC}[n(\mathbf{r})]$ and hence $V_{XC}(\mathbf{r})$
- The functional was partitioned so that $E_{XC}[n(\mathbf{r})]$ would be a (relativly) small contribution
- Use an approximation
  - Local Density Approximation (LDA)
  - Generalised Gradient Approximation (GGA)
    - PW91, PBE, BLYP, B3LYP and so on . . .
- Parameterised on Quantum Monte Carlo results
- *Ab initio* GGAs are generally better for energies, and not worse for structures

Solving an eigenproblem in a basis

- We have a problem of the form:

$$\hat{H}|\psi_i\rangle = \epsilon_i|\psi_i\rangle$$

- The wavefunctions are orthonormal:

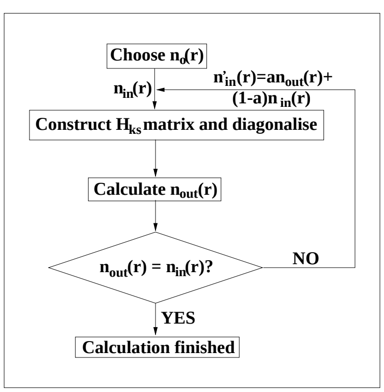
$$\langle\psi_i|\psi_j\rangle = \delta_{ij}$$

- If we choose a basis, we can construct a Hamiltonian as a matrix and diagonalise

energy level $\rightarrow$ eigenvalue
wavefunction/orbital $\rightarrow$ eigenvector

Being (self) consistent

- $V_H(\mathbf{r})$ and $V_{XC}(\mathbf{r})$ depend on $n(\mathbf{r})$
- $n(\mathbf{r})$ depends on $\{\psi_i(\mathbf{r})\}$
- But we are trying to find $\{\psi_i(\mathbf{r})\}$ and the corresponding energy levels — we need *self-consistency*



Just a few atoms

- Use a local basis set
  - possibly based on atomic orbitals
  - maybe some mathematically simple set like gaussians
- Build the Hamiltonian matrix
- Diagonalise
- This scales at $O(N^3)$

In a crystal

- Crystals contain $\approx 10^{23}$ atoms
- Direct diagonalisation of even a cluster of 10^3 atoms would be very costly
- So is it impossible?
- No!! Use symmetry . . .
  - crystals have translational symmetry (definition)
  - symmetry leads to a new quantum number, $\mathbf{k}$
  - use periodic boundary condition (PBCs) and you just have to worry about the atoms in the unit cell of the crystal

Periodic boundary conditions

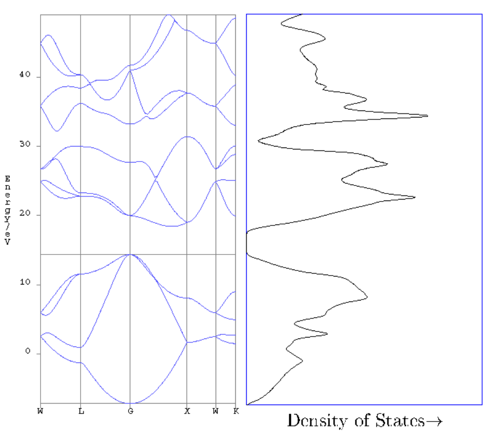
- Leads to Bloch's Theorem

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}} U_{n\mathbf{k}}(\mathbf{r})$$

$$U_{n\mathbf{k}}(\mathbf{r}) = U_{n\mathbf{k}}(\mathbf{r}+\mathbf{R})$$

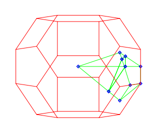
- For an extended system
  - Transforms problem from solving infinite number of states to one of discrete bands and infinite number of $\mathbf{k}$-points.
  - but $E(\mathbf{k})$ etc. is smooth, so evaluate at relatively small number of $\mathbf{k}$-points
- $\mathbf{k}$-point sampling becomes an issue
- Metals require very high sampling density

The bandstructure picture

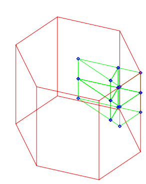


- A band-structure plot for diamond compared with the total density of states

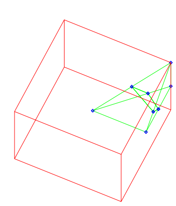
FCC



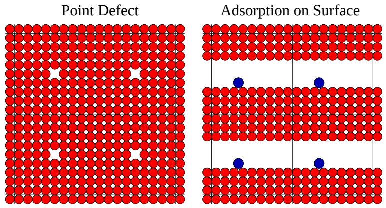
Hexagonal



Simple Cubic



The Super-cell approximation

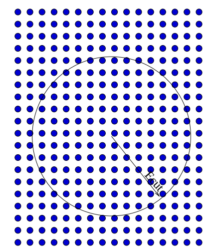


- Aperiodic systems can also be treated within periodic boundary conditions
- The super-cell chosen must be large enough that the properties of interest are converged with respect to cell size

Planewaves: the natural basis set

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}}U_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} U^{\mathbf{G}}_{n\mathbf{k}} e^{i(\mathbf{G}+\mathbf{k}).\mathbf{r}}$$

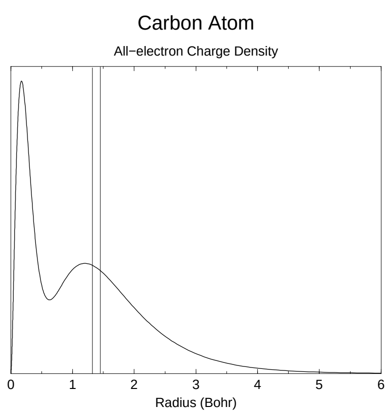
- The natural basis set for a crystal
- PBCs lead to a discrete set
- Cutoff energy defines set - convergence well defined



- Advantages - FFTs, force calculation, orthogonality and simplicity
- Disadvantages - BIG

Core and Valence electrons

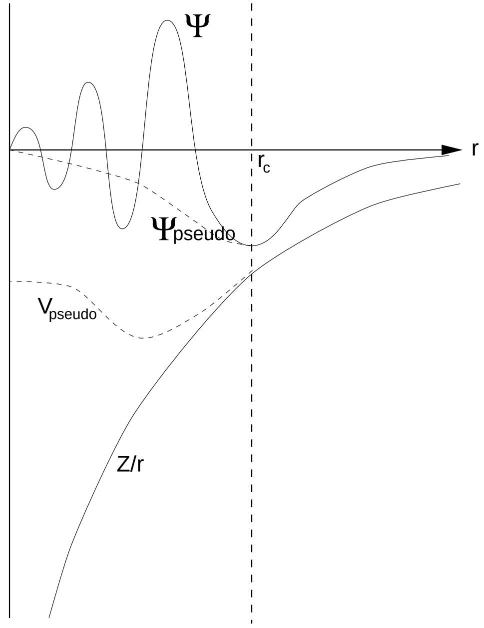
- Core electrons don't take part in bonding (definition!)



Level	Energy(Ry)	Occupation
1s	-19.90408	2.000
2s	-1.00279	2.000
2p	-0.39838	2.000

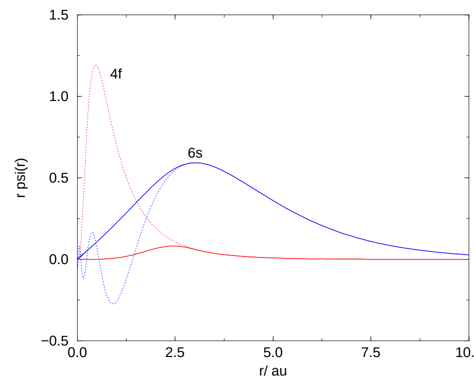
Pseudopotentials

- Too many planewaves needed for core states, and related orthogonality
- Physical properties depend on valence electrons - throw away cores
- Pseudopotential constructed so that
  - Scattering properties preserved
  - Potential and Ψ identical outside core
  - Norm conserved (can be relaxed)
- Transferability . . .
- Local/Non-local and realspace potentials . . .



Ultrasoft Pseudopotentials

- Relax norm conservation - soft for 2p,3d,4f
- Augment - to replace lost charge
- Multiple projectors at any energy
- Accurate, soft and transferable



Pseudized and all electron valence states for Lutetium

There is a lot more ...

- Conventional diagonalisation is too slow
- We can calculate forces and stresses directly
- And we can calculate many other properties
- All this and more in the next lectures
- But does it work?

Material	Expt	Theory	Delta	Type
LaBi	6.57	6.648	1.2%	alloy
$IrAl_3$(a)	4.246	4.2	-1.1%	alloy
$IrAl_3$(c)	7.756	7.618	-1.8%	alloy
NiAs(a)	3.602	3.549	-1.5%	alloy
NiAs(c)	5.009	5.031	0.4%	alloy
NpAs	3.31	3.415	3.1%	alloy
YPo	6.251	6.288	0.6%	alloy
$RuAs_2$(a)	5.4279	5.34	-1.6%	alloy
$RuAs_2$(b)	6.1834	6.13	-0.9%	alloy
$RuAs_2$(c)	2.9685	2.985	0.6%	alloy
Sc_3In(a)	6.421	6.418	0.0%	alloy
Sc_3In(c)	5.183	5.183	0.0%	alloy
CaF_2	5.4626	5.496	0.6%	halide
BCl_3(a)	6.08	6.216	2.2%	halide
BCl_3(c)	6.55	6.632	1.2%	halide
LiBr	5.489	5.467	-0.4%	halide
CsCl	4.123	4.167	1.1%	halide
LiI	6	6	0.0%	halide
KF	5.33	5.354	0.4%	halide
KrF2	1.89	1.916	1.4%	halide
LiI	3.5092	3.45	-1.7%	halide
NaI	6.462	6.537	1.1%	halide
RbBr	6.86	6.979	1.7%	halide
TlCl	3.835	3.875	1.0%	halide
YF_3(a)	6.353	6.362	0.1%	halide
YF_3(b)	6.85	6.903	0.8%	halide
YF_3(c)	4.393	4.471	1.7%	halide
Ag	4.086	4.112	0.6%	metal
Al	4.0495	3.965	-2.1%	metal
As(a)	3.7595	3.7048	-1.5%	metal
As(c)	10.4573	10.0825	-3.7%	metal
Au	4.0783	4.1528	1.8%	metal
Ba	5.019	4.992	-0.5%	metal
Be(a)	2.2856	2.2788	-0.3%	metal
Be(c)	3.5832	3.579	-0.1%	metal
C(a)	2.46	2.439	-0.9%	metal
C(c)	6.8	7.109	4.3%	metal
Ca	5.582	5.506	-1.4%	metal
Cd(a)	2.9788	3.035	1.9%	metal
Cd(c)	5.6167	5.665	0.9%	metal

Material	Expt	Theory	Delta	Type
Co(a)	2.507	2.481	-1.0%	metal
Co(c)	4.069	4.018	-1.3%	metal
Co	3.544	3.494	-1.4%	metal
Cr	2.8846	2.8509	-1.2%	metal
Cr_3Si	4.555	4.525	-0.7%	metal
Cs	6.14	6.14	0.0%	metal
Cu	3.6147	3.631	0.4%	metal
Fe	2.8664	2.8826	0.6%	metal
Hf(a)	3.1946	3.082	-3.7%	metal
Hf(c)	5.0511	4.9605	-1.8%	metal
Ir	3.8389	3.8547	0.4%	metal
K	5.32	5.311	-0.2%	metal
La(a)	3.77	3.824	1.4%	metal
La(c)	12.131	12.539	3.3%	metal
Mg(a)	3.2094	3.209	0.0%	metal
Mg(c)	5.2105	5.21	0.0%	metal
Mo	3.1469	3.1588	0.4%	metal
Na	4.2906	4.312	0.5%	metal
Nb	3.3006	3.3153	0.4%	metal
Ni	3.524	3.5	-0.7%	metal
Os(a)	2.7353	2.7455	0.4%	metal
Os(c)	4.3191	4.3339	0.3%	metal
Pb	4.9502	5.046	1.9%	metal
Pd	3.8907	3.903	0.3%	metal
Po	3.345	3.308	-1.1%	metal
Pt	3.9239	3.971	1.2%	metal
Rb	5.7	5.7	0.0%	metal
Re(a)	2.76	2.758	-0.1%	metal
Re(c)	4.458	4.446	-0.3%	metal
Rh	3.8044	3.853	1.3%	metal
Ru(a)	2.7058	2.72	0.5%	metal
Ru(c)	4.2816	4.289	0.2%	metal
Sc(a)	3.308	3.309	0.0%	metal
Sc(c)	5.2653	5.178	-1.7%	metal
Sn	6.4912	6.408	-1.3%	metal
Sr	6.0849	6.085	0.0%	metal
Ta	3.3026	3.2522	-1.5%	metal
Tc(a)	2.735	2.751	0.6%	metal
Tc(c)	4.388	4.392	0.1%	metal
Te(a)	4.456	4.437	-0.4%	metal
Te(c)	5.921	5.9	-0.4%	metal

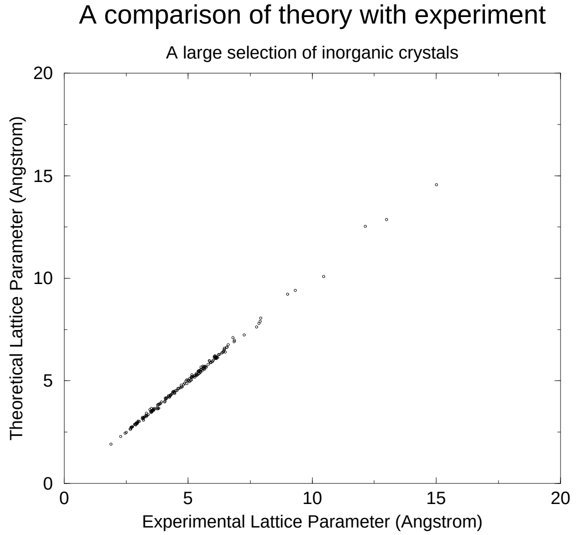
Material	Expt	Theory	Delta	Type
Ti(a)	2.9506	2.936	-0.5%	metal
Ti(c)	4.6788	4.658	-0.4%	metal
Tl(a)	3.4566	3.5948	3.8%	metal
Tl(c)	5.5248	5.5436	0.3%	metal
V	3.028	3.019	-0.3%	metal
W	3.165	3.222	1.8%	metal
Y(a)	3.6451	3.6376	-0.2%	metal
Y(c)	5.7305	5.672	-1.0%	metal
Zn(a)	2.6649	2.641	-0.9%	metal
Zn(c)	4.9468	4.865	-1.7%	metal
Zr(a)	3.2312	3.2411	0.3%	metal
Zr(c)	5.1477	5.2055	1.1%	metal
CsH	6.387	6.387	0.0%	misc
$HfGe_2$(a)	3.8154	3.665	-4.1%	misc
$HfGe_2$(b)	15.004	14.567	-3.0%	misc
$HfGe_2$(c)	3.7798	3.635	-4.0%	misc
$LaTiO_3$(a)	5.6253	5.602	-0.4%	misc
$LaTiO_3$(b)	5.5918	5.712	2.1%	misc
$LaTiO_3$(c)	7.9047	7.899	-0.1%	misc
MnB_4(a)	5.5029	5.427	-1.4%	misc
MnB_4(b)	5.3669	5.278	-1.7%	misc
MnB_4(c)	2.9487	2.914	-1.2%	misc
ZrN	4.62	4.634	0.3%	misc
OsP_2(a)	5.1012	5.05	-1.0%	misc
OsP_2(b)	5.9022	5.8886	-0.2%	misc
OsP_2(c)	2.9183	2.9366	0.6%	misc
PtS(a)	3.48	3.515	1.0%	misc
PtS(c)	6.11	6.12	0.2%	misc
Re_3B(a)	2.89	2.889	0.0%	misc
Re_3B(b)	9.313	9.405	1.0%	misc
Re_3B(c)	7.258	7.235	-0.3%	misc
$RhTe_2$	6.4394	6.48	0.6%	misc
$TcOF_4$(a)	9	9.22	2.4%	misc
$TcOF_4$(c)	7.92	8.05	1.6%	misc
UN_2	5.31	5.254	-1.1%	misc
UC_2(a)	3.517	3.524	0.2%	misc
UC_2(c)	5.987	5.946	-0.7%	misc
VN	4.13	4.137	0.2%	misc
WC(a)	2.906	2.949	1.5%	misc
WC(c)	2.837	2.873	1.3%	misc
Ag_2O	4.72	4.788	1.4%	oxide

Material	Expt	Theory	Delta	Type
Al_2O_3(a)	4.759	4.703	-1.2%	oxide
Al_2O_3(c)	12.991	12.871	-0.9%	oxide
BaO	5.523	5.562	0.7%	oxide
BeO(a)	2.6979	2.738	1.5%	oxide
BeO(c)	4.3772	4.446	1.5%	oxide
BiOF(a)	3.7469	3.633	-3.1%	oxide
BiOF(c)	6.226	6.267	0.7%	oxide
Bi_2O_3	5.45	5.36	-1.7%	oxide
CaO	4.8105	4.817	0.1%	oxide
Cu_2O	4.2696	4.2533	-0.4%	oxide
HgO(a)	6.6129	6.756	2.1%	oxide
HgO(b)	5.52	5.668	2.6%	oxide
HgO(c)	3.5219	3.65	3.5%	oxide
MgO	4.2112	4.277	1.5%	oxide
NbO	4.2103	4.2344	0.6%	oxide
SiO_2(a)	4.91	4.987	1.5%	oxide
SiO_2(c)	5.402	5.459	1.0%	oxide
SnO_2(a)	4.7373	4.709	-0.6%	oxide
SnO_2(c)	3.1864	3.15	-1.2%	oxide
SrO	5.13	5.17	0.8%	oxide
TaO	4.422	4.49	1.5%	oxide
TiO_2(a)	4.594	4.625	0.7%	oxide
TiO_2(c)	2.959	2.965	0.2%	oxide
ZrO_2	5.07	5.116	0.9%	oxide
Ar	5.256	5.256	0.0%	rare
He(a)	3.555	3.556	0.0%	rare
He(c)	5.798	5.798	0.0%	rare
Ne	4.462	4.38	-1.9%	rare
Ra	5.148	5.288	2.6%	rare
GaAs	5.653	5.663	0.2%	semiconductor
BN	3.615	3.598	-0.5%	semiconductor
BeS	4.855	4.871	0.3%	semiconductor
C(diamond)	3.556	3.539	-0.5%	semiconductor
CdSe	6.05	6.146	1.6%	semiconductor
GaN	4.5	4.535	0.8%	semiconductor
GaP	5.4505	5.4956	0.8%	semiconductor
Ge	5.6575	5.572	-1.5%	semiconductor
HgTe	6.4623	6.585	1.9%	semiconductor
HgS	5.8517	5.978	2.1%	semiconductor
HgSe	6.084	6.211	2.0%	semiconductor
InAs	6.05838	6.1808	2.0%	semiconductor

Material	Expt	Theory	Delta	Type
InP	5.86875	5.9489	1.3%	semiconductor
PbSe	6.128	6.1508	0.4%	semiconductor
GaSb	6.0954	6.1323	0.6%	semiconductor
AlSb	6.1355	6.078	-0.9%	semiconductor
ZnSe	5.6676	5.7113	0.8%	semiconductor
BeSe	5.139	5.194	1.1%	semiconductor
Si	5.4307	5.44	0.2%	semiconductor
ZnTe	6.101	6.142	0.7%	semiconductor
ZnS	5.4193	5.4839	1.2%	semiconductor
$CoSi_2$	5.36	5.3	-1.1%	silicide
$FeSi_2$(a)	2.684	2.649	-1.3%	silicide
$FeSi_2$(c)	5.128	5.037	-1.8%	silicide
$MoSi_2$(a)	3.2	3.195	-0.2%	silicide
$MoSi_2$(c)	7.85	7.791	-0.8%	silicide
PdSi(a)	5.6173	5.6123	-0.1%	silicide
PdSi(b)	3.3909	3.3514	-1.2%	silicide
PdSi(c)	6.1534	6.1534	0.0%	silicide

Milman, Winkler, White, Pickard, Payne, Akhmatskaya, and Nobes.
Electronic structure, properties and phase stability of inorganic crystals: The pseudopotential plane-wave approach.
International Journal of Quantum Chemistry, **77**:895-910, 2000.

- We got all this from
  - Schrödinger's Equation
  - a many-body uniform electron gas
  - some clever approximations



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