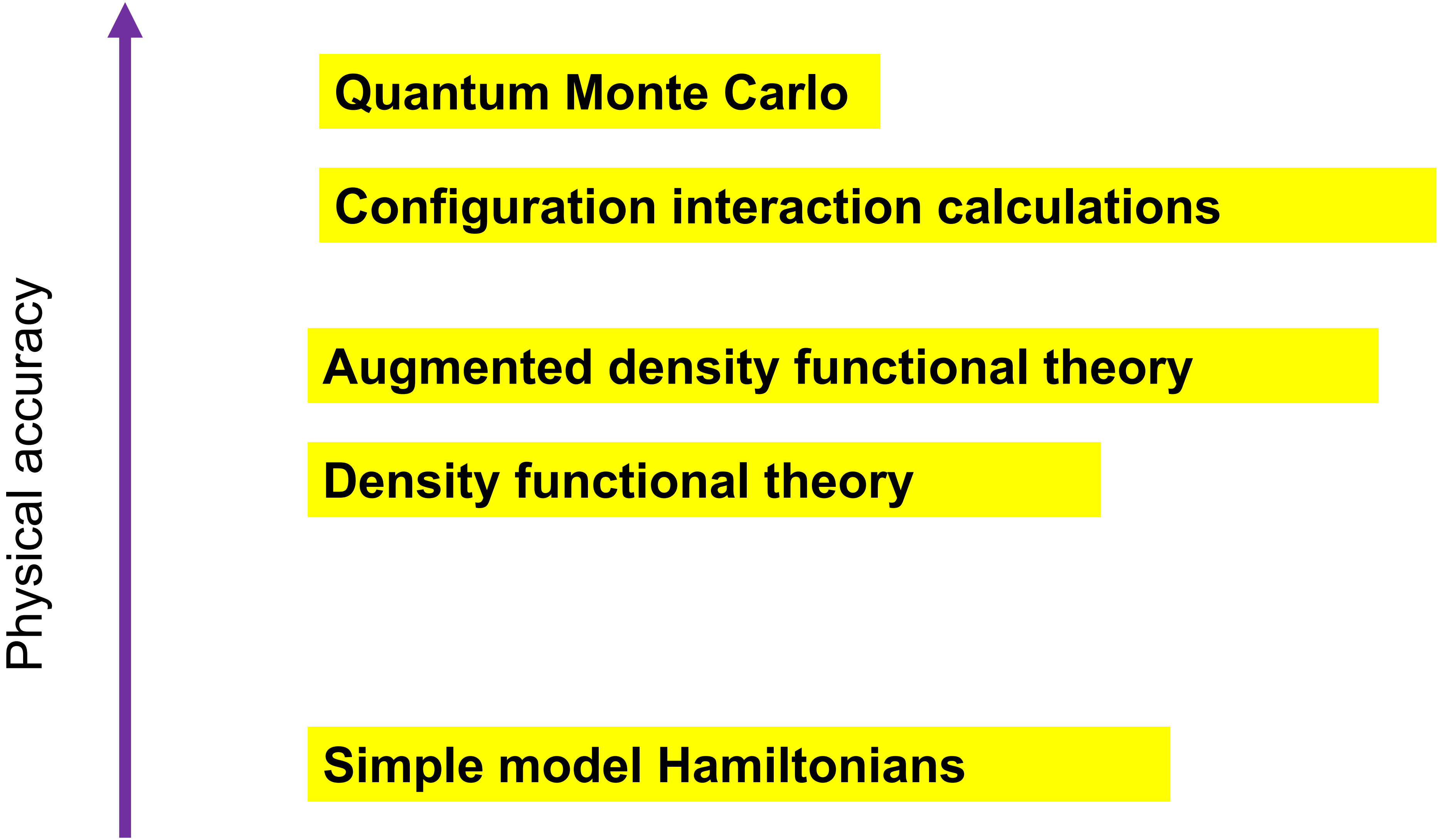
Density functional theory and its role in condensed matter physics

A discussion on the use of density functional theory (DFT) in computational modeling.

- ☐ To place DFT on the list of tools that can be used to analyze condensed matter materials, amplifying its strengths and weaknesses and comparing with some of the other tools
- ☐ To discuss the variety of computer codes available that implement DFT and their reliability
- ☐ To discuss DFT's role in explaining/predicting experimental measurements. Often it is the case that what is easy to compute may be difficult to measure and vise versa

Natalie’s opinion – subject to rotten tomatoes



Physical accuracy

Quantum Monte Carlo

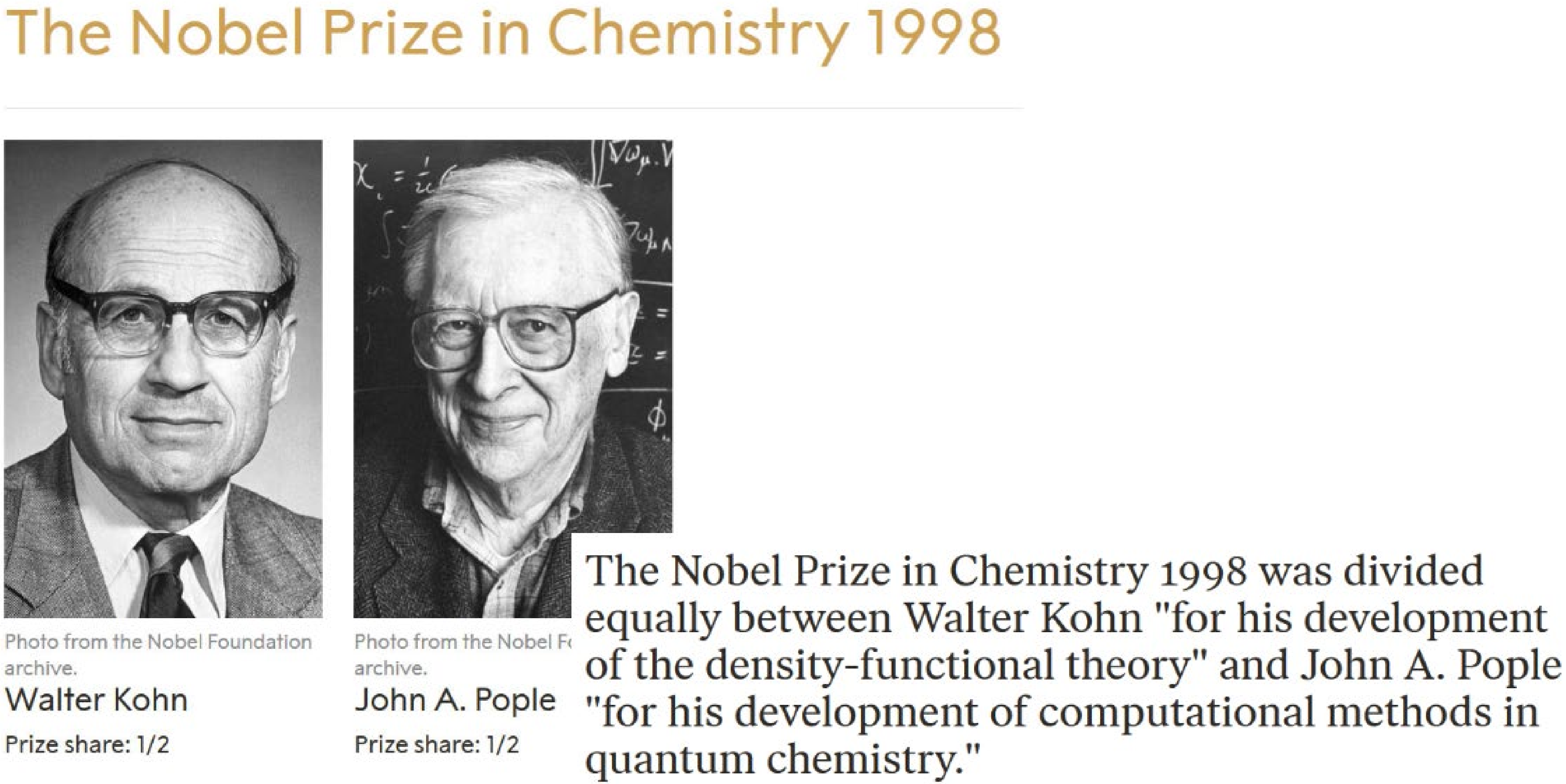
Configuration interaction calculations

Augmented density functional theory

Density functional theory

Simple model Hamiltonians

Brief history



The Nobel Prize in Chemistry 1998

Photo from the Nobel Foundation archive.

Walter Kohn

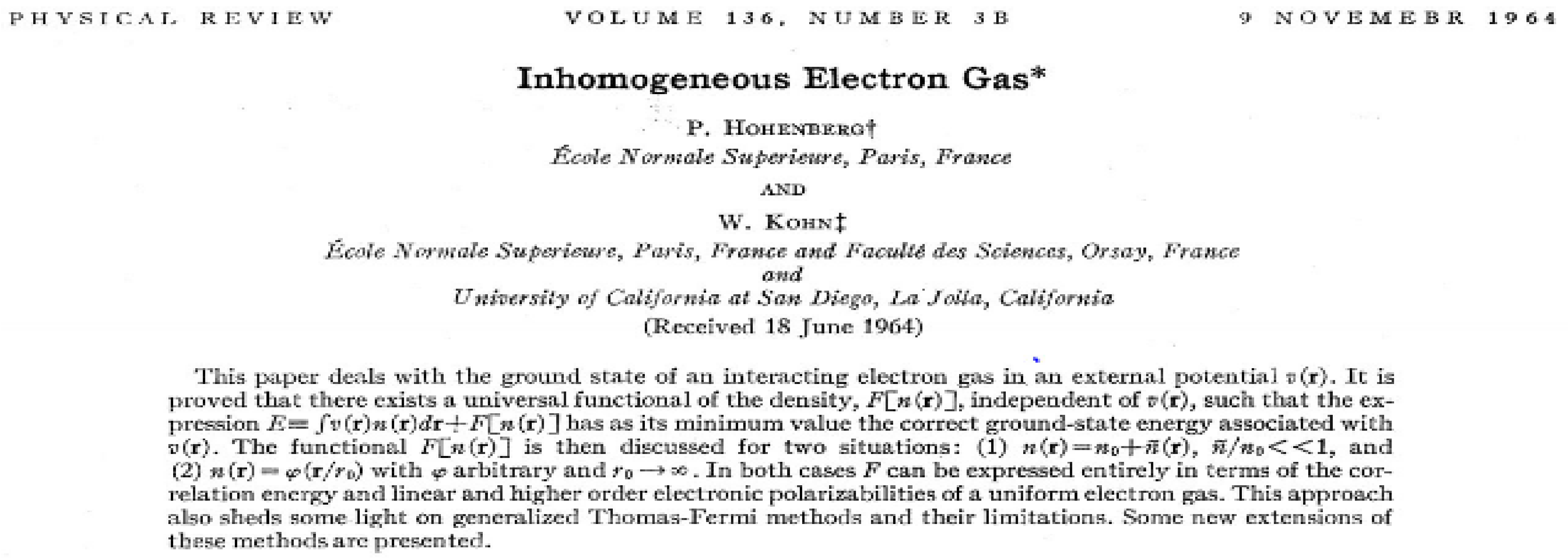
Prize share: 1/2

Photo from the Nobel F archive.

John A. Pople

Prize share: 1/2

The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn "for his development of the density-functional theory" and John A. Pople "for his development of computational methods in quantum chemistry."



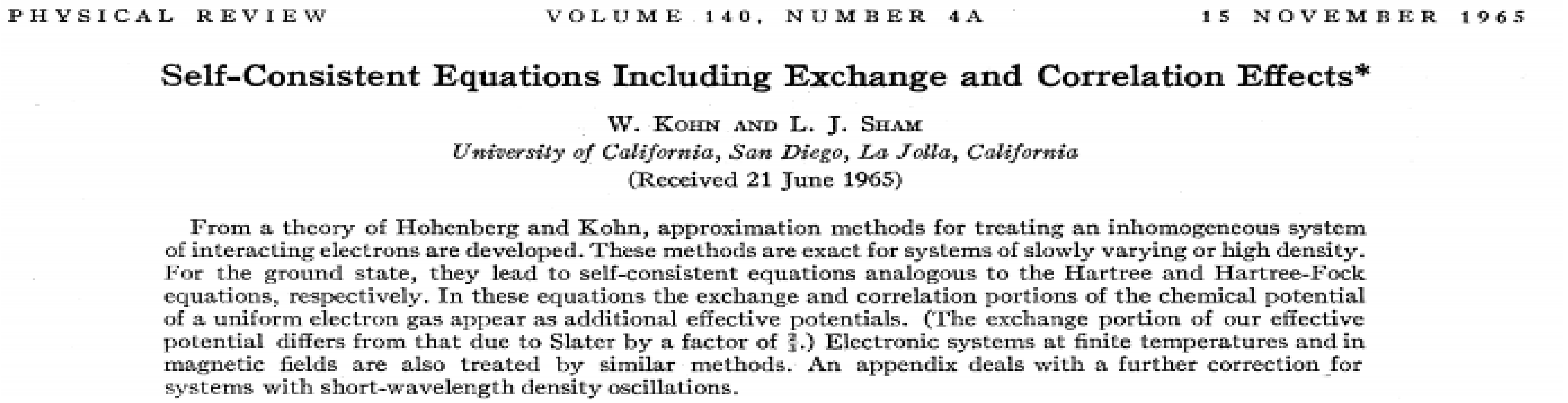
PHYSICAL REVIEW VOLUME 136, NUMBER 3B 9 NOVEMEBR 1964

Inhomogeneous Electron Gas*

P. HOHENBERG†
École Normale Superieure, Paris, France
AND
W. KOHN‡
École Normale Superieure, Paris, France and Faculté des Sciences, Orsay, France
and
University of California at San Diego, La Jolla, California

(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r})=n_0+\tilde{n}(\mathbf{r})$, $\tilde{n}/n_0<<1$, and (2) $n(\mathbf{r})=\varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0\rightarrow\infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.



PHYSICAL REVIEW VOLUME 140, NUMBER 4A 15 NOVEMBER 1965

Self-Consistent Equations Including Exchange and Correlation Effects*

W. KOHN AND L. J. SHAM
University of California, San Diego, La Jolla, California

(Received 21 June 1965)

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of $\frac{2}{3}$.) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

Earlier story based on many electron atoms – Hartree-Fock theory

A wavefunction representing N indistinguisable Fermi particles must have the property:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, ..\mathbf{r}_i ... \mathbf{r}_j ... \mathbf{r}_N) = -\psi(\mathbf{r}_1, \mathbf{r}_2, ..\mathbf{r}_j ... \mathbf{r}_i ... \mathbf{r}_N)$$

If the wavefunction can be represented as products of N single particle states

$\varphi_a(\mathbf{r}), \varphi_b(\mathbf{r}), \varphi_c(\mathbf{r})....$, the following construction has the correct antisymmetry property --

Example for N particles using Slater determinant:

$$\psi(\mathbf{r}_1, \mathbf{r}_2....\mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_a(\mathbf{r}_1) & \varphi_a(\mathbf{r}_2) & \varphi_a(\mathbf{r}_3) & \cdots & \varphi_a(\mathbf{r}_N) \\ \varphi_b(\mathbf{r}_1) & \varphi_b(\mathbf{r}_2) & \varphi_b(\mathbf{r}_3) & \cdots & \varphi_b(\mathbf{r}_N) \\ \varphi_c(\mathbf{r}_1) & \varphi_c(\mathbf{r}_2) & \varphi_c(\mathbf{r}_3) & \cdots & \varphi_c(\mathbf{r}_N) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \varphi_z(\mathbf{r}_1) & \varphi_z(\mathbf{r}_2) & \varphi_z(\mathbf{r}_3) & \cdots & \varphi_z(\mathbf{r}_N) \end{vmatrix}$$

For an atom of atomic number *Z* and *N* electrons, the Hamiltonian for the electrons of mass *m* is:

$$H(\mathbf{r}_1, \mathbf{r}_2 \ldots \mathbf{r}_N) = \sum_{i=1}^{N} \left(-\frac{\hbar^2 \nabla_i^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_i} + \frac{e^2}{8\pi\epsilon_0} \sum_{j \neq i} \frac{1}{\left| \mathbf{r}_i - \mathbf{r}_j \right|} \right)$$

$$\equiv H_{kin} + H_{n-e} + H_{e-e}$$

Note that the nuclear-electron interaction term $H_{n\text{-}e}$ is often called the "external" interaction in DFT. Also note that the electron-electron repulsion term $H_{e\text{-}e}$ excludes the "self" electron-electron interaction.

If the single particle basis functions $\varphi_a(\mathbf{r}_i)$ are orthogonal to each other, the expection value of the Hamiltonian can be written in terms of single particle and two particle matrix elements:

$$h_{aa} = \int d^3r \left|\varphi_a(\mathbf{r})\right|^2 \left(-\frac{\hbar^2\nabla^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r} \right)$$

$$v_{abcd} = \frac{e^2}{4\pi\epsilon_0} \iint d^3r_i d^3r_j \;\; \frac{\varphi_a(\mathbf{r}_i)\varphi_b^*(\mathbf{r}_i)\varphi_c(\mathbf{r}_j)\varphi_d^*(\mathbf{r}_j)}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

The expectation value of the Hamiltonian for the Slater determinant wavefunction is then

$$\left\langle \Psi \middle| H \middle| \Psi \right\rangle = \sum_{a=1}^{N} h_{aa} + \frac{1}{2} \sum_{a,b=1}^{N} \left(v_{aabb} - v_{abab} \right)$$

Hartree term

Exchange term

An estimate of the total energy of the system is obtained by optimizing $\frac{\left\langle \Psi \middle| H \middle| \Psi \right\rangle}{\left\langle \Psi \middle| \Psi \right\rangle}$ with respect to $\{\varphi_a, \varphi_b \ldots\}$

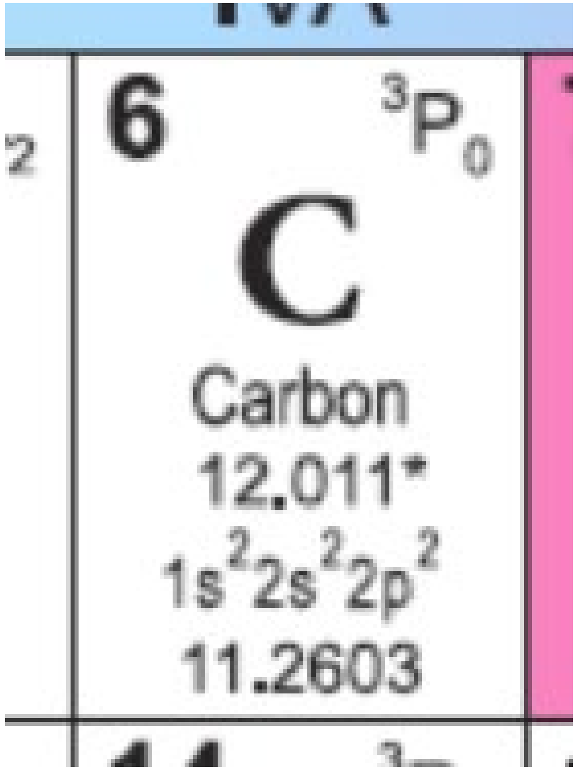
Comments --

$$\langle \Psi | H | \Psi \rangle = \sum_{a=1}^{N} h_{aa} + \frac{1}{2} \sum_{a,b=1}^{N} \left(\underset{\underset{\text{Hartree term}}{\Uparrow}}{v_{aabb}} - \underset{\underset{\text{Exchange term}}{\Uparrow}}{v_{abab}} \right)$$

- Note that in this single Slater determinant formulation, the "self interaction" term automatically cancels out of the calculation.
- **The term "electron correlation" is (often/always) defined to be additional energy estimated beyond the single Slater determinant or Hartree-Fock analysis.**
- Extensions of this idea using a linear combination of Slater determinant have been extensively explored.

Illustration for an atomic system

Consider the case of a single atom, choosing the coordinate system at the center of the nucleus. We will further assume that the atom is spherically symmetric, averaging over the multiplet configurations.



$$n(\mathbf{r}) = n(r)$$

$$\phi_i(\mathbf{r}) = \phi_{n_i l_i}(r) Y_{l_i m_i}(\hat{\mathbf{r}})$$

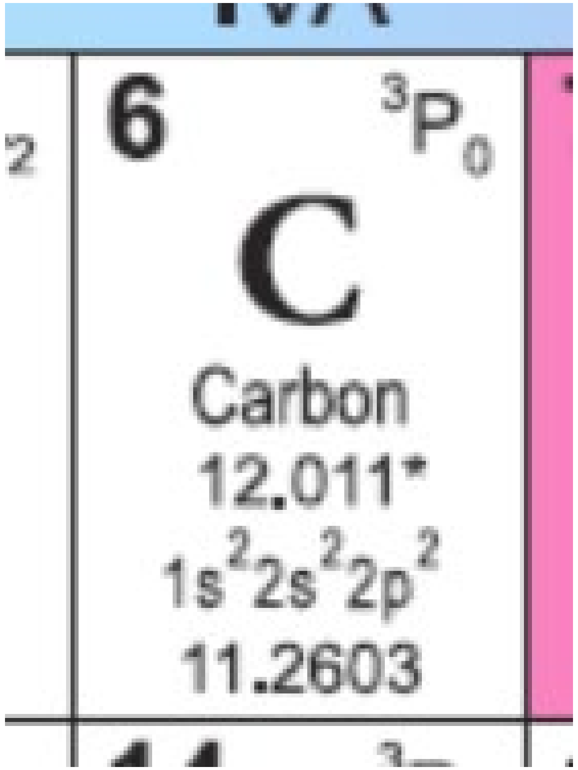
$$n(r) = 4\pi \sum_i w_{n_i l_i} \left| \phi_{n_i l_i}(r) \right|^2$$

$$\text{where } \; 0 \le w_{n_i l_i} \le 2(2l_i + 1)$$

For spherically symmetric atom:

$$\phi_{n_i l_i m_i}(\mathbf{r}) = \phi_{n_i l_i}(r) Y_{l_i m_i}(\hat{\mathbf{r}})$$

$$\phi_{n_i l_i}(r) = \frac{P_{n_i l_i}(r)}{r}$$



6

$^3P_0$

C

Carbon

12.011*

$1s^2 2s^2 2p^2$

11.2603

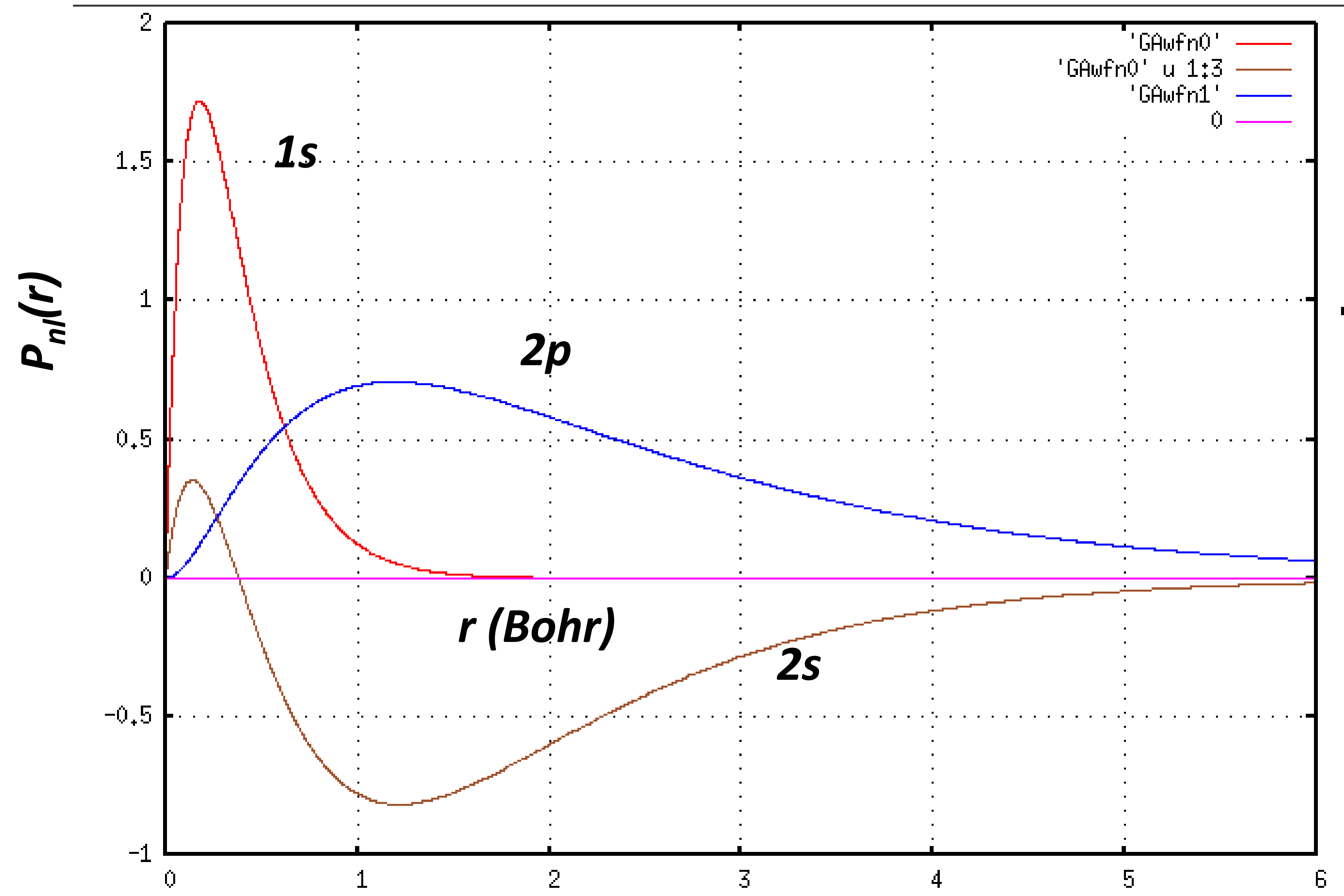
Example for carbon

$$n(r) = \sum_i w_{n_i l_i} \left|\phi_{n_i l_i}(r)\right|^2$$

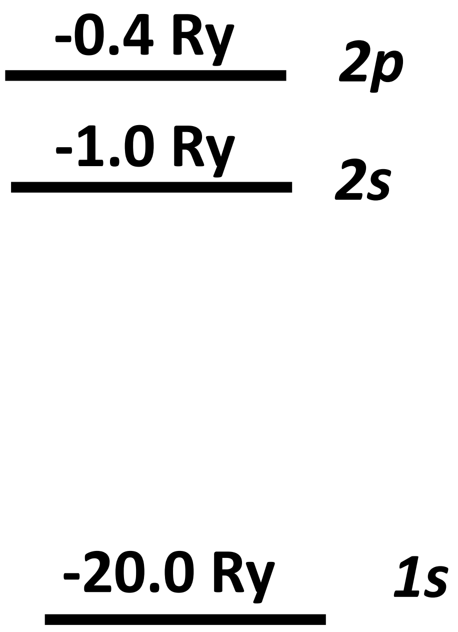
$$= 4\pi\left(2\left|\phi_{1s}(r)\right|^2 + 2\left|\phi_{2s}(r)\right|^2 + 2\left|\phi_{2p}(r)\right|^2\right)$$

$$= \frac{4\pi}{r^2}\left(2\left|P_{1s}(r)\right|^2 + 2\left|P_{2s}(r)\right|^2 + 2\left|P_{2p}(r)\right|^2\right)$$

Results for carbon

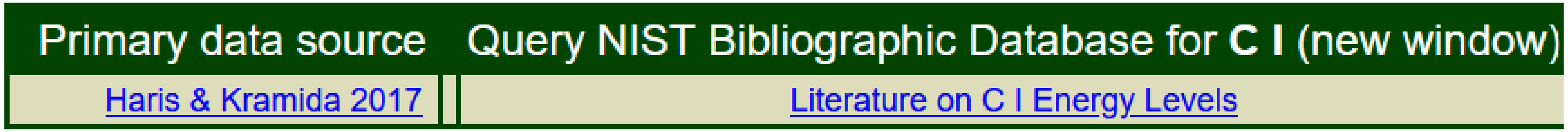


Lagrange multipliers

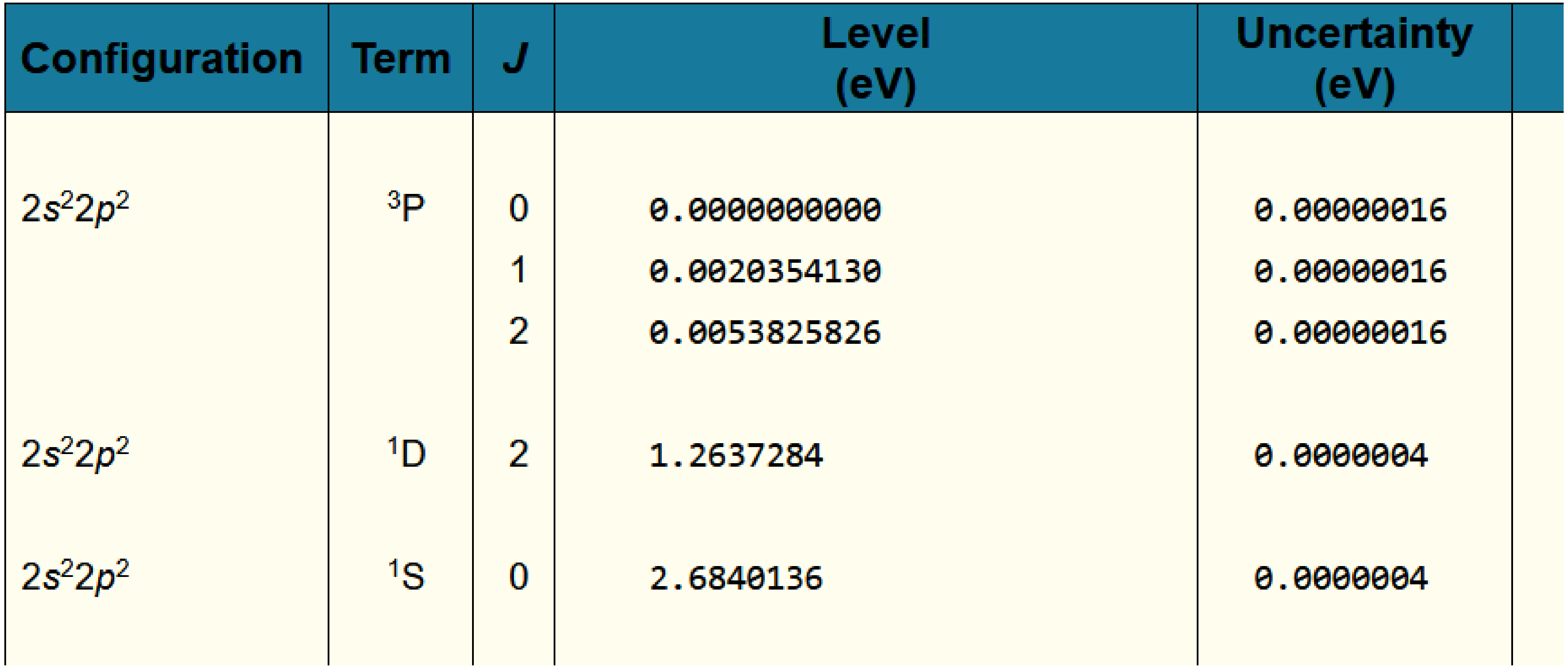


Note that this is not what is seen experimentally. However, as shown by Condon & Shortley in 1950's, starting with the simple spherically symmetric picture, one can use degenerate perturbation theory to analyze the effects of the detailed electron-electron interactions. From https://physics.nist.gov/PhysRefData/ASD/levels_form.html

Carbon energy levels

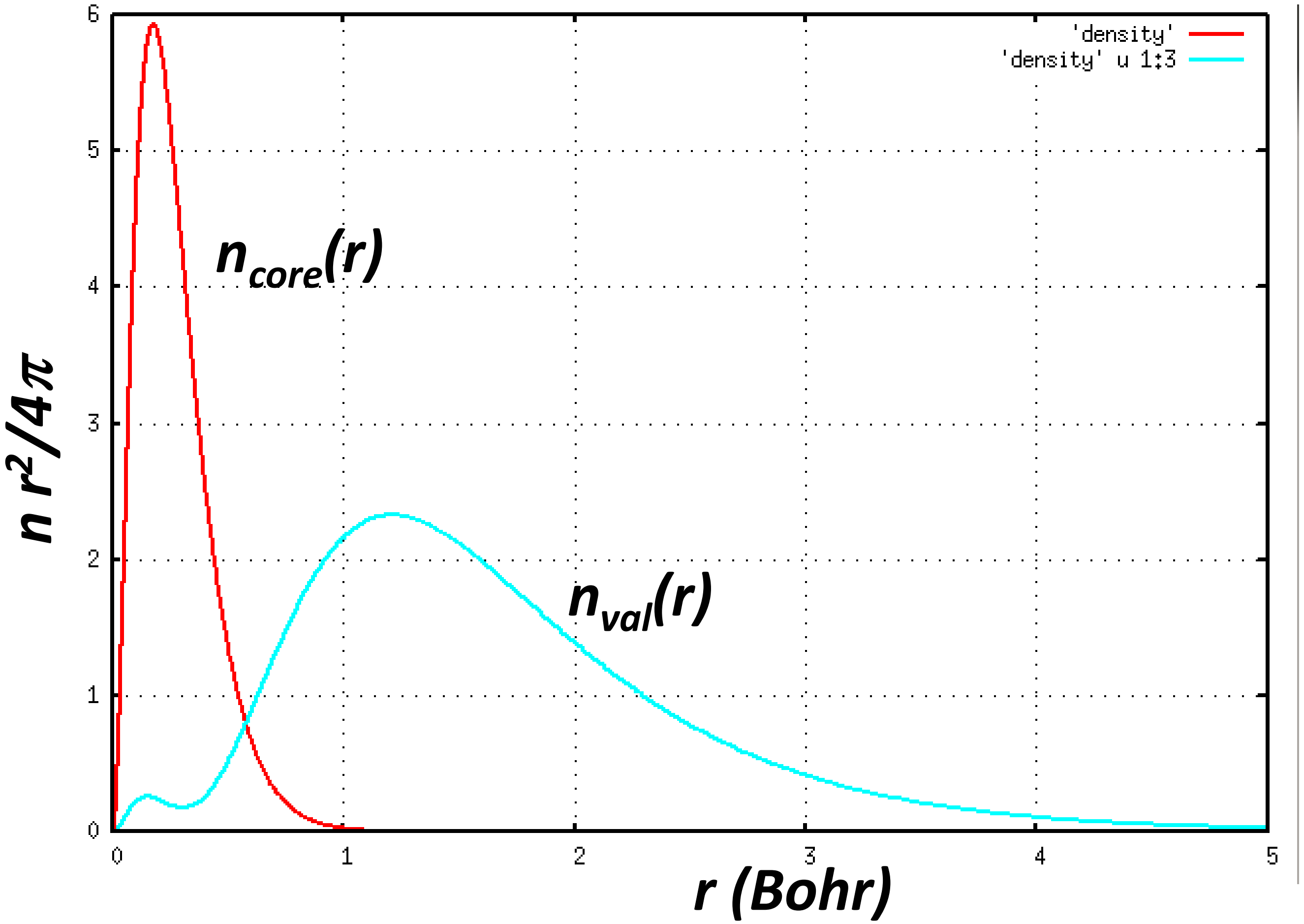


Primary data source	Query NIST Bibliographic Database for **C I** (new window)
Haris & Kramida 2017	Literature on C I Energy Levels



Configuration	Term	*J*	Level (eV)	Uncertainty (eV)
$2s^22p^2$	^{3}P	0	0.0000000000	0.00000016
		1	0.0020354130	0.00000016
		2	0.0053825826	0.00000016
$2s^22p^2$	^{1}D	2	1.2637284	0.0000004
$2s^22p^2$	^{1}S	0	2.6840136	0.0000004

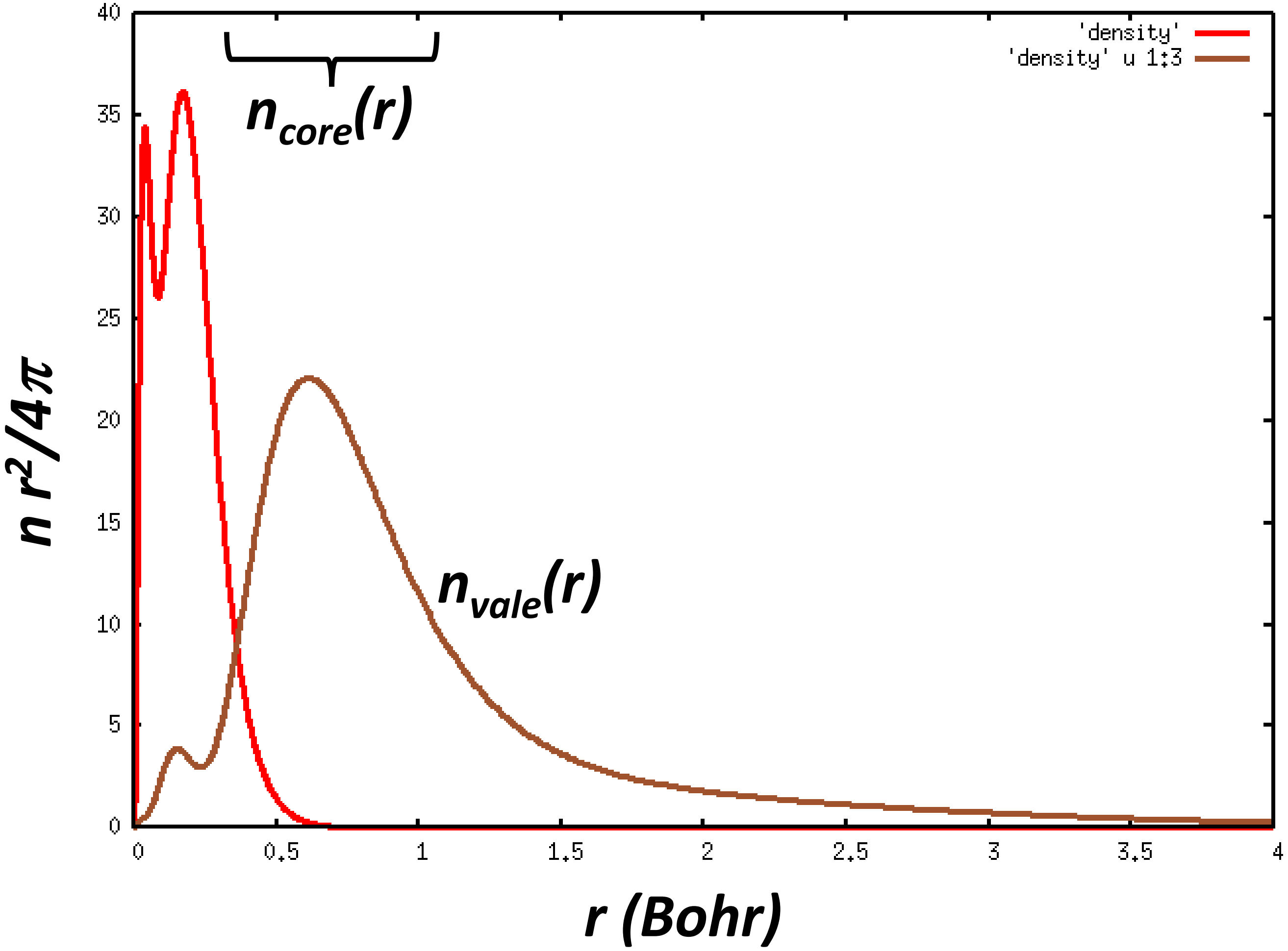
Electron density

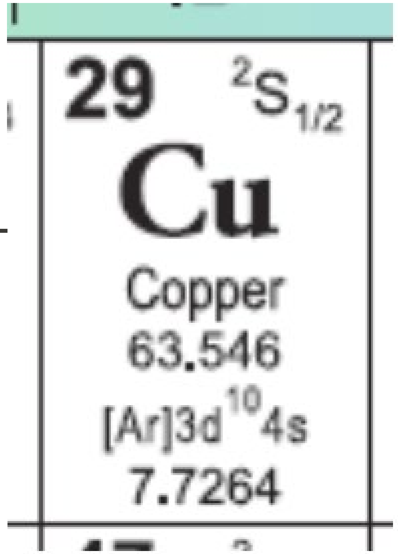


➔**Frozen core approximation**

Example for Cu

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$





Density functional theory approach – for the same Hamiltonian

$$H(\mathbf{r}_1,\mathbf{r}_2\ldots\mathbf{r}_N)=\sum_{i=1}^{N}\left(-\frac{\hbar^2\nabla_i^2}{2m}-\frac{Ze^2}{4\pi\epsilon_0 r_i}+\frac{e^2}{8\pi\epsilon_0}\sum_{j\neq i}\frac{1}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}\right)$$

$$E_{\text{tot}}=\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}=E_{\text{tot}}(n)=E_{\text{kin}}(n)+E_{\text{ext}}(n)+E_{\text{Hartree}}(n)+E_{\text{x}}(n)+E_{\text{c}}(n)$$

Optimized
expectation
value

Extra
correlation
term

$$E_{\text{Hartree}}(n)=\frac{e^2}{4\pi\epsilon_0}\iint d^3r\,d^3r'\,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Estimate of the exchange contribution

$$E_{\text{x}}=-\frac{e^2}{8\pi\epsilon_0}\sum_{i,j}\delta_{\sigma_i\sigma_j}\int d^3r\,\phi_{n_i\mathbf{k}_i\sigma_i}{}^{*}(\mathbf{r})\phi_{n_j\mathbf{k}_j\sigma_j}(\mathbf{r})\int d^3r'\,\frac{\phi_{n_j\mathbf{k}_j\sigma_j}{}^{*}(\mathbf{r}')\phi_{n_i\mathbf{k}_\mathbf{i}\sigma_i}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

For jellium:

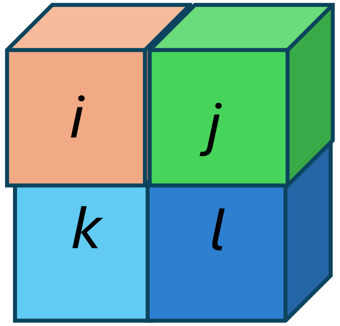
It can be shown that

$$\phi_{n_j\mathbf{k}_j\sigma_j}(\mathbf{r})=\frac{1}{\sqrt{\mathcal{V}}}e^{i\mathbf{k}_j\cdot\mathbf{r}}$$

$$E_{\text{x}}(n)=-\frac{2e^2k_F^4}{4\pi\epsilon_0(2\pi)^3}=-\frac{2e^2\left(3\pi^2n\right)^{4/3}}{4\pi\epsilon_0(2\pi)^3}=-\frac{3e^2n}{4\pi\epsilon_0 4\pi}\left(3\pi^2n\right)^{1/3}$$

Digression on spatially varying electron density

$$k_F^i = \left(3\pi^2 n_i\right)^{1/3}$$



$$\Rightarrow \quad k_F(\mathbf{r}) = \left(3\pi^2 n(\mathbf{r})\right)^{1/3}$$

For a free electron system of N spin 1/2 particles, the Fermi sphere times 2 can accomodate those electrons:

$$\frac{\Omega}{(2\pi)^3} 2 \left(\frac{4\pi k_F^3}{3}\right) = N \qquad k_F = \left(3\pi^2 \frac{N}{\Omega}\right)^{1/3} \equiv \left(3\pi^2 n\right)^{1/3}$$

Total electronic energy as a function of the electron density

$$E_{\mathrm{tot}}(n) = E_{\mathrm{kin}}(n) + E_{\mathrm{ext}}(n) + E_{\mathrm{Hartree}}(n) + E_{\mathrm{x}}(n) + E_{\mathrm{c}}(n)$$

$$E_{\mathrm{ext}}(n) = \int d^3r V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r})$$

$E_{\mathrm{xc}}(n) \equiv E_{\mathrm{x}}(n) + E_{\mathrm{c}}(n)$ -- many possibilities -- LDA, GGA, PBESOL, R2SCAN01.....

plus perhaps Van der Waals interactions?

Brief and simplified statement of density functional theory thanks to Kohn & Sham--

Given $V_{\mathrm{ext}}(\mathbf{r})$ and the form of $E_{\mathrm{tot}}(n)$, there is a unique $n(\mathbf{r})$ that minimizes $E_{\mathrm{tot}}(n)$

Practical equations for evaluating density functional theory

Effective single-particle equations with eigenstates $\varphi_i(\mathbf{r})$ and Lagrange mutipliers ϵ_i (which are used to constrain normalization):

$$H_{eff}(\mathbf{r})\varphi_i(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \right)\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r})$$

At self-consistency, $n(\mathbf{r}) = \sum_i \left|\varphi_i(\mathbf{r})\right|^2$ and $E_{tot}\left(n(\mathbf{r})\right)$ is optimized

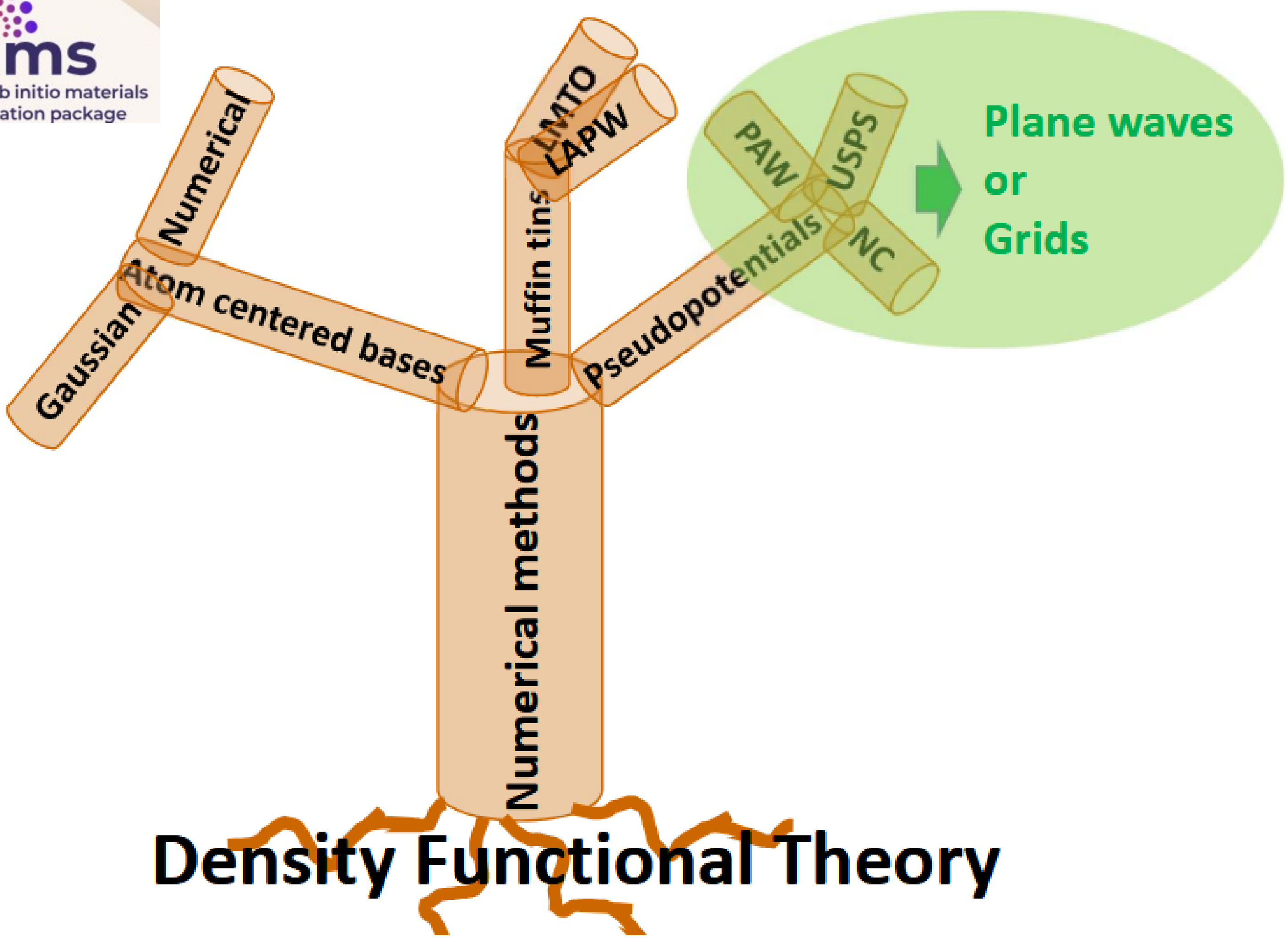
and determines a good estimate of the ground state energy of the system.

Comments

- ❑ Self-interaction energy no longer cancels in E_{Hartree} and E_{x} **and remains a serious problem.**
- ❑ E_{xc} is still (always) under development
- ❑ Extension of the non-relativistic treatment to the Dirac equations and the so-called “scalar relativistic” treatments as well as to “generalized” Kohn-Sham equations when the exchange-correlation for contains kinetic energy density terms.
- ❑ Lagrange multipliers ε_i are **not** energy levels …..
- ❑ In this context, density functional theory only applies to the treatment of the electrons. For molecular materials, solids, and liquids, the Born-Oppenheimer approximation must be used. In many cases, it is reasonable to treat the nuclei with the classical equations of motion. However, quantizing the linearized nuclear displacements leads to good estimates of the phonon spectrum.
- ❑ Estimates of electronic excitations, can be made by performing DFT with constraints.

Some of the many numerical implementations of density functional theory

FHI-aims
The ab initio materials simulation package

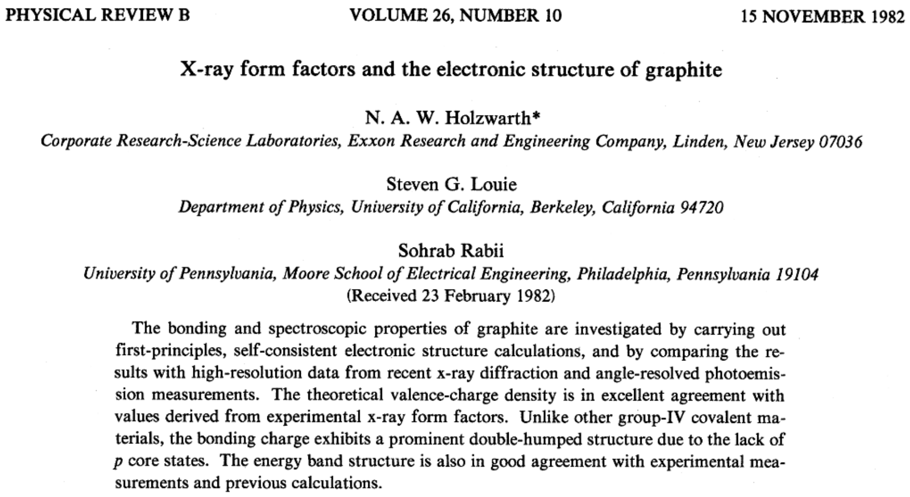


Abinit gui

QUANTUMESPRESSO

An example of a moderately successful DFT calculation --

Comparison with measured electron density reconstructed from X-ray analysis



PHYSICAL REVIEW B VOLUME 26, NUMBER 10 15 NOVEMBER 1982

X-ray form factors and the electronic structure of graphite

N. A. W. Holzwarth*
Corporate Research-Science Laboratories, Exxon Research and Engineering Company, Linden, New Jersey 07036

Steven G. Louie
Department of Physics, University of California, Berkeley, California 94720

Sohrab Rabii
University of Pennsylvania, Moore School of Electrical Engineering, Philadelphia, Pennsylvania 19104

(Received 23 February 1982)

The bonding and spectroscopic properties of graphite are investigated by carrying out first-principles, self-consistent electronic structure calculations, and by comparing the results with high-resolution data from recent x-ray diffraction and angle-resolved photoemission measurements. The theoretical valence-charge density is in excellent agreement with values derived from experimental x-ray form factors. Unlike other group-IV covalent materials, the bonding charge exhibits a prominent double-humped structure due to the lack of *p* core states. The energy band structure is also in good agreement with experimental measurements and previous calculations.

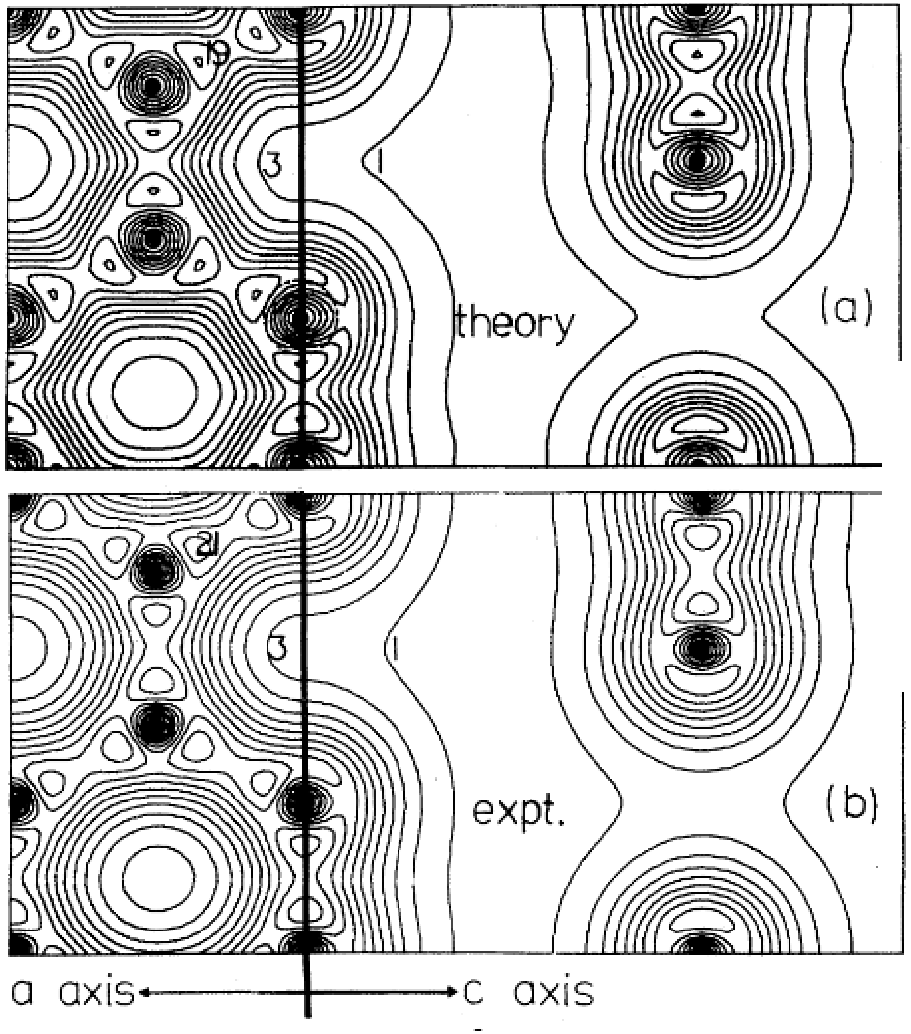
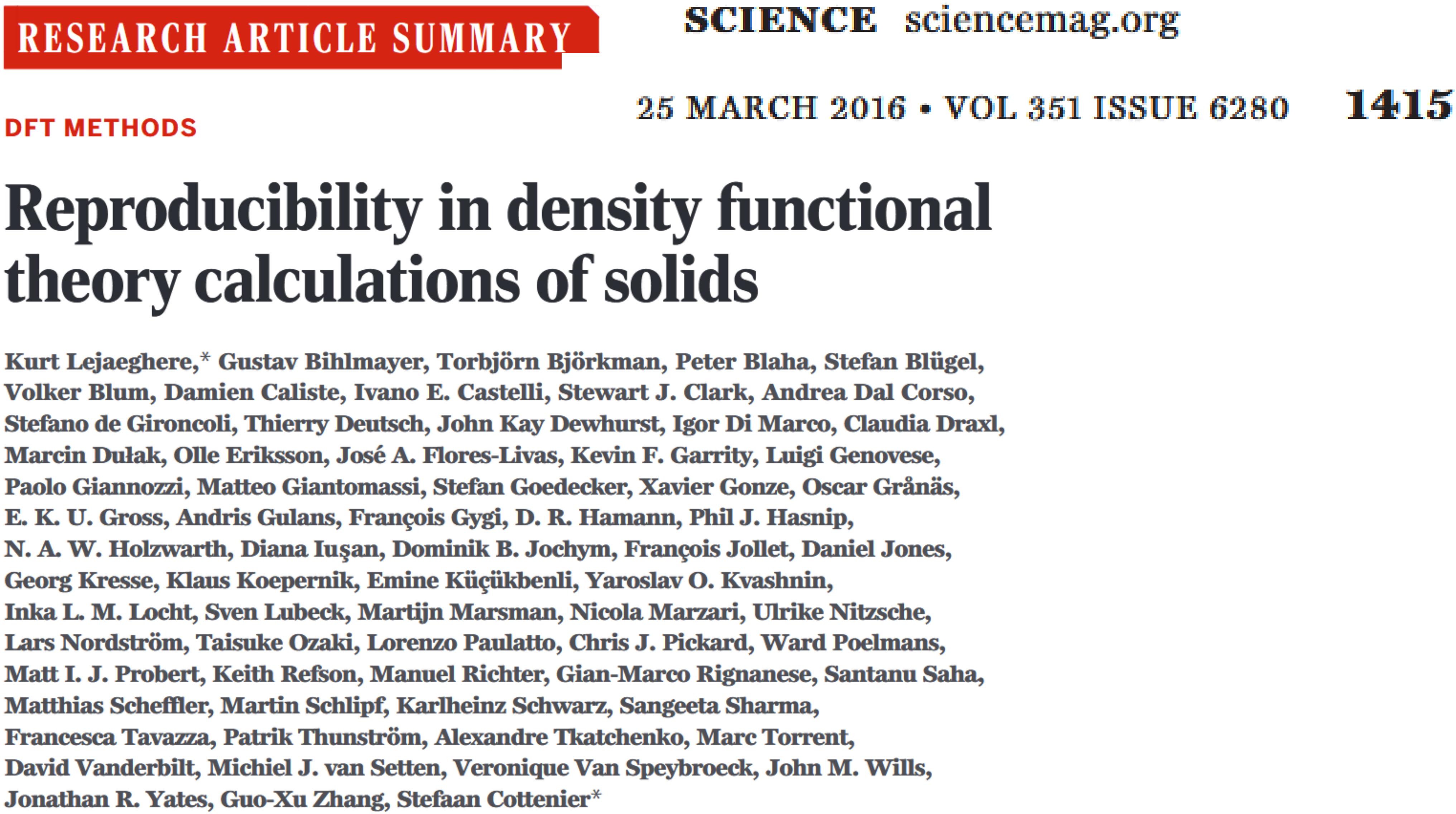


FIG. 1. Contour plots of valence-electronic-charge density for graphite: (a) Present results, and (b) results from analysis of x-ray data by Chen, Trucano, and Stewart (Ref. 1). Contour values are given in units of $0.1e/\text{Å}^3$. Atomic positions are denoted by filled circles. Two planes are shown—one containing an *a* axis and the other containing the *c* axis and both intersecting at 90° along a C—C bond. In (a) the dashed circle denotes the pesudopotential radius. In (b) the authors quote a standard deviation of $\pm 0.1e/\text{Å}^3$.

Attempts to estimate the reproducibility of DFT calculations --



RESEARCH ARTICLE SUMMARY

SCIENCE sciencemag.org

25 MARCH 2016 • VOL 351 ISSUE 6280 1415

DFT METHODS

Reproducibility in density functional theory calculations of solids

Kurt Lejaeghere,* Gustav Bihlmayer, Torbjörn Björkman, Peter Blaha, Stefan Blügel, Volker Blum, Damien Caliste, Ivano E. Castelli, Stewart J. Clark, Andrea Dal Corso, Stefano de Gironcoli, Thierry Deutsch, John Kay Dewhurst, Igor Di Marco, Claudia Draxl, Marcin Dułak, Olle Eriksson, José A. Flores-Livas, Kevin F. Garrity, Luigi Genovese, Paolo Giannozzi, Matteo Giantomassi, Stefan Goedecker, Xavier Gonze, Oscar Grånäs, E. K. U. Gross, Andris Gulans, François Gygi, D. R. Hamann, Phil J. Hasnip, N. A. W. Holzwarth, Diana Iuşan, Dominik B. Jochym, François Jollet, Daniel Jones, Georg Kresse, Klaus Koepernik, Emine Küçükbenli, Yaroslav O. Kvashnin, Inka L. M. Locht, Sven Lubeck, Martijn Marsman, Nicola Marzari, Ulrike Nitzsche, Lars Nordström, Taisuke Ozaki, Lorenzo Paulatto, Chris J. Pickard, Ward Poelmans, Matt I. J. Probert, Keith Refson, Manuel Richter, Gian-Marco Rignanese, Santanu Saha, Matthias Scheffler, Martin Schlipf, Karlheinz Schwarz, Sangeeta Sharma, Francesca Tavazza, Patrik Thunström, Alexandre Tkatchenko, Marc Torrent, David Vanderbilt, Michiel J. van Setten, Veronique Van Speybroeck, John M. Wills, Jonathan R. Yates, Guo-Xu Zhang, Stefaan Cottenier*

Si lattice constant

(figure from Science paper)

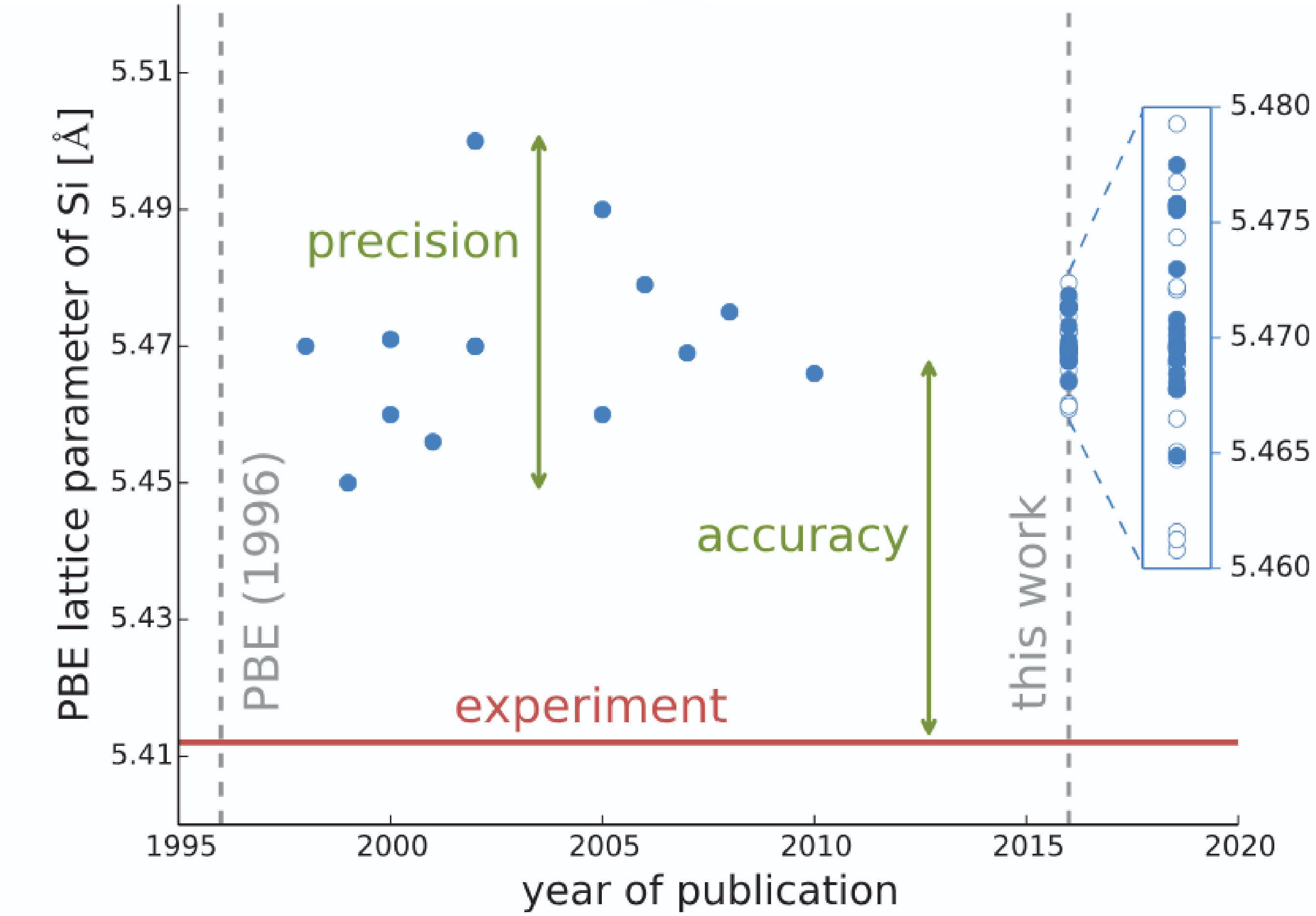


Fig. 1. Historical evolution of the predicted equilibrium lattice parameter for silicon. All data points represent calculations within the DFT-PBE framework. Values from literature (data points before 2016) (*15*, *16*, *18*, *56*–*62*, *63*–*65*) are compared with (i) predictions from the different codes used in this study (2016 data points, magnified in the inset; open circles indicate data produced by older methods or calculations with lower numerical settings) and (ii) the experimental value, extrapolated to 0 K and corrected for zero-point effects (red line) (*26*). The concepts of precision and accuracy are illustrated graphically.

How do the results from independent codes compare?

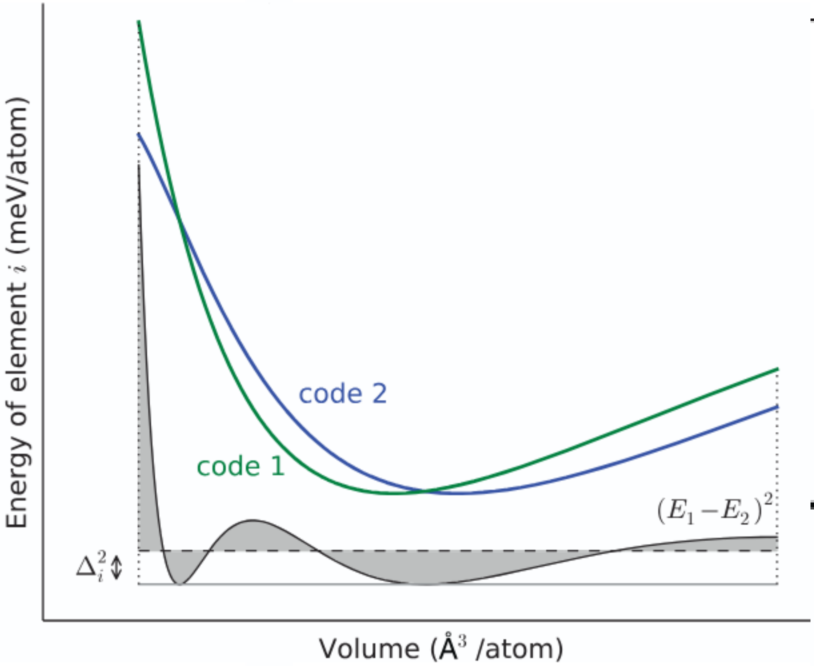
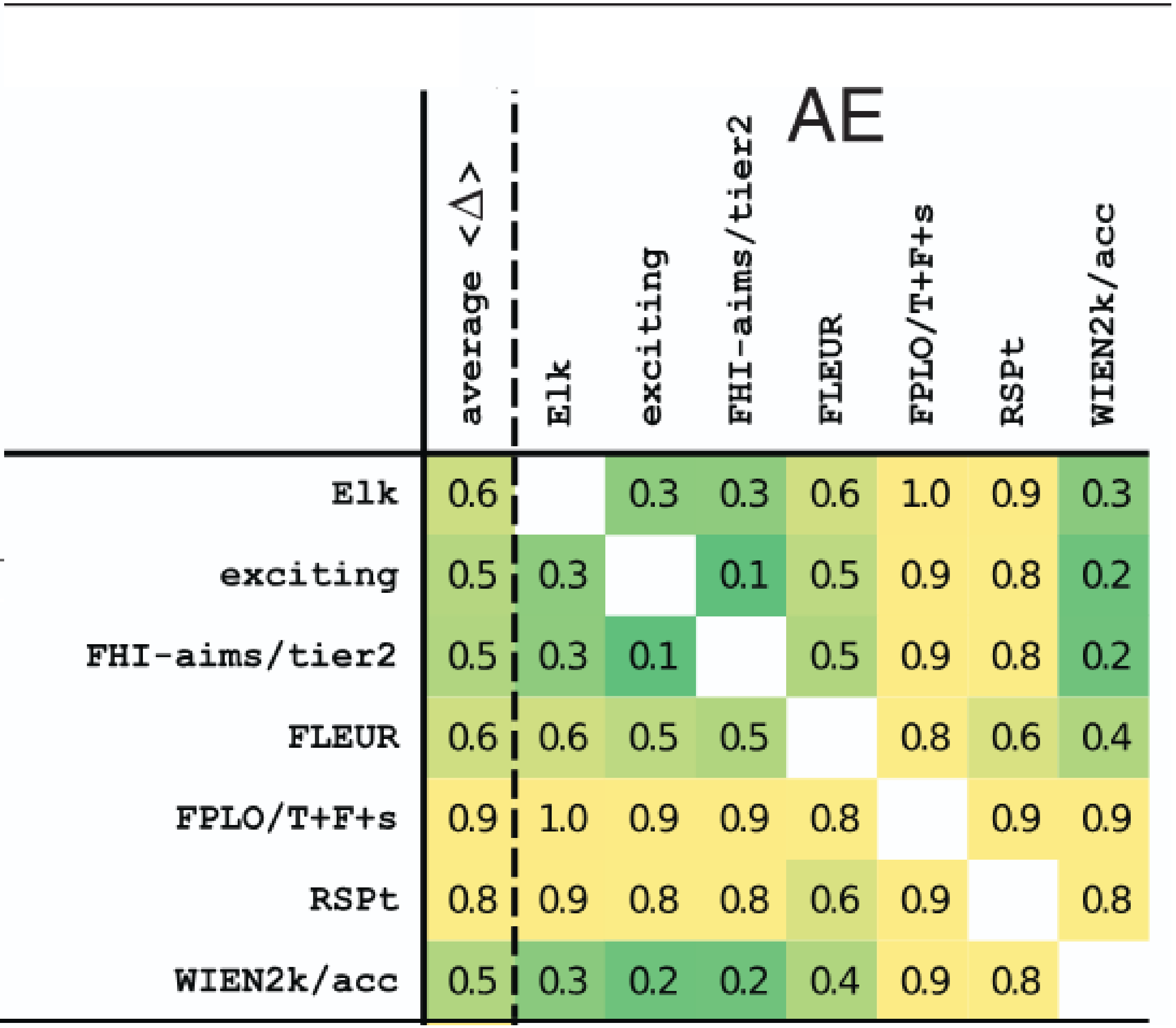


Fig. 3. Graphical representation of the Δ gauge. The black curve depicts the quadratic energy difference between two EOS [$(E_1 - E_2)^2$, where the subscripts correspond to the two codes shown], and Δ_i corresponds to the root-mean-square average. This is demonstrated by the shaded area, which is equally large above and below the Δ_i^2 line.



AE

AE	average <Δ>	Elk	exciting	FHI-aims/tier2	FLEUR	FPLO/T+F+s	RSPt	WIEN2k/acc
Elk	0.6		0.3	0.3	0.6	1.0	0.9	0.3
exciting	0.5	0.3		0.1	0.5	0.9	0.8	0.2
FHI-aims/tier2	0.5	0.3	0.1		0.5	0.9	0.8	0.2
FLEUR	0.6	0.6	0.5	0.5		0.8	0.6	0.4
FPLO/T+F+s	0.9	1.0	0.9	0.9	0.8		0.9	0.9
RSPt	0.8	0.9	0.8	0.8	0.6	0.9		0.8
WIEN2k/acc	0.5	0.3	0.2	0.2	0.4	0.9	0.8	

(Figures from Science paper)

Conclusions

- ❑ Density functional theory is a good starting point for the analysis of many condensed matter systems – especially for exploring properties associated with the electronic ground state.
- ❑ It is important to continually scrutinize the physical and numerical approximations made while applying the formalism
- ❑ Become an active user of one or more software packages and perhaps develop your own codes
- ❑ Is it better for experimentalists to perform their own simulations or to collaborate with computationally focused colleagues?

Thank you!