Introduction to DFT and its Application to Defects in Semiconductors

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The Future: Computer-Aided Materials Design

- Can access the space of materials not experimentally known
- Can scan through structures and compositions faster than is possible experimentally
- Unbiased search can yield unintuitive solutions

- Can accelerate the discovery and deployment of new materials

Accurate electronic structure methods

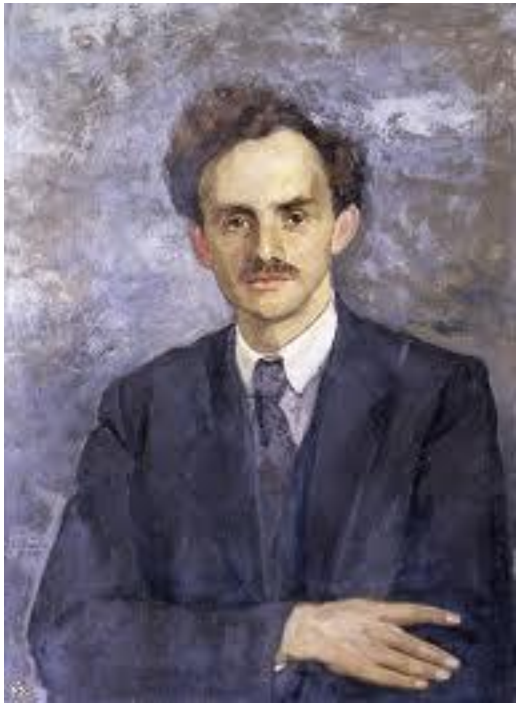
+

Efficient search algorithms

Dirac's Challenge

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus *completely known*, and the difficulty is only that the exact application of these laws leads to equations *much too complicated to be soluble*. It therefore becomes desirable that *approximate* practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems ... "

-P. A. M. Dirac, 1929



P. A. M. Dirac

Physics Nobel Prize, 1933

The Many (Many, Many) Body Problem

Schrödinger's Equation:

$$i\hbar\frac{\partial}{\partial t}\Psi = H\Psi \qquad H = -\frac{\hbar^2}{2m}\sum_{n=1}^{N}\nabla_n^2 + V\left(\vec{r}_1, \vec{r}_2 \ldots, \vec{r}_N, t\right)$$

The physical laws are completely known

But…

There are as many electrons in a penny as stars in the known universe!

Electronic Structure Methods for Materials Properties

Structure
Mechanical properties
Vibrational spectrum

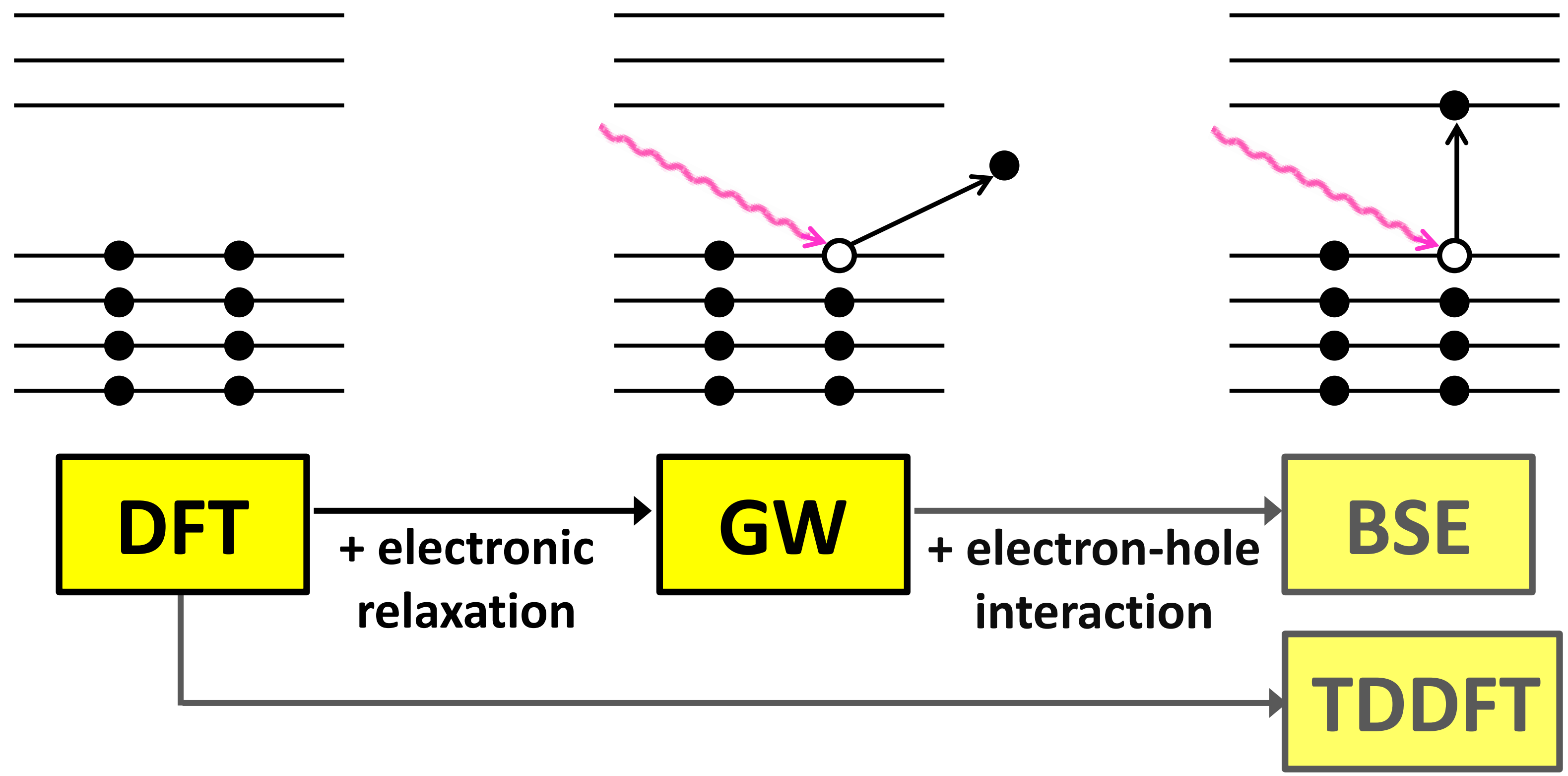
Ground State

Ionization potential (IP)
Electron Affinity (EA)
Fundamental gap
Defect/dopant charge transition levels

Charged Excitation

Absorption spectrum
Optical gap
Exciton binding energy

Neutral Excitation



DFT

+ electronic relaxation

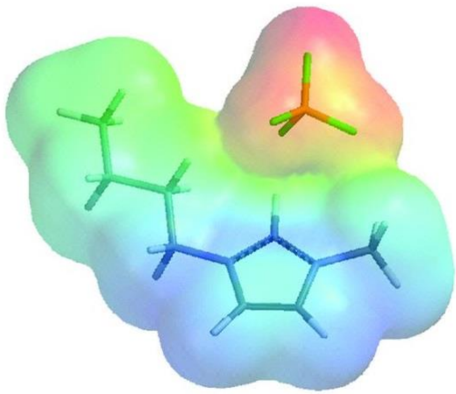
GW

+ electron-hole interaction

BSE

TDDFT

DFT- Density Functional Theory



Use what you can measure!

The density is used as the basic variable instead of the many-body wave function with no loss of information

The Hohenberg & Kohn theorem (1964):

One-to-one correspondence between the ground state density and the external potential

Walter Kohn

Nobel Prize in Chemistry, 1998

For DFT

3 $n(r) \longleftrightarrow V_{ext}(r) \longleftrightarrow \psi(r_1, r_2, \ldots, r_n)$ **3N**

Electron Density

ion-e

Many-body wave function

DFT- Density Functional Theory

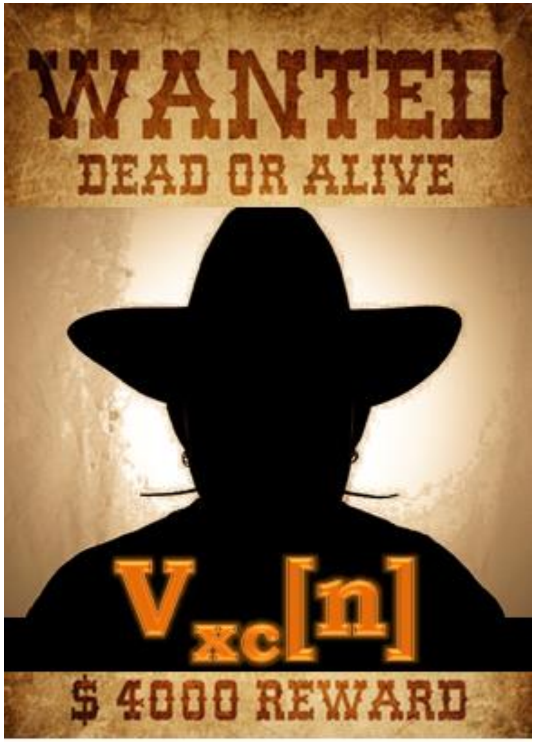
Exact mapping to a single particle problem with the many-body effects contained in the <u>exchange-correlation functional</u>

Kohn & Sham, 1965

$$\left\{ {}^{-\nabla^2}\!/_{2} + V_{ion}(\boldsymbol{r}) + V_{Hartree}[n(\boldsymbol{r})] + V_{xc}[n(\boldsymbol{r})]\right\}\varphi_i(\boldsymbol{r}) = \varepsilon_i\varphi_i(\boldsymbol{r})$$

kinetic **ion-e** **e-e** **many-body**

$$n(\boldsymbol{r}) = \sum_{\substack{occupied\\ states}} |\varphi_i(\boldsymbol{r})|^2$$



The Kohn-Sham equation is a Schrödinger-like eigenvalue equation, solved self-consistently to find the ground state density

V_{xc} is unknown and must be approximated

DFT- Density Functional Theory

The success of DFT calculations hinges on a good choice of approximation for the exchange-correlation functional

DFT Functionals: Local and Semi-Local Functionals

The local density approximation (LDA) E_{xc} is approximated by its value per particle in a uniform electron gas weighted by the local density

$$E_{xc}^{LDA}[n]=\int d^3r\, n(\vec{r})\,\varepsilon_{xc}^{unif}(n(\vec{r}))$$

D. M. Ceperley , B. J. Alder, *Phys. Rev. Lett.* 45, 566 (1980)

Generalized gradient approximation (GGA) E_{xc} includes a dependence on the density gradient to account for density variations (PBE)

J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996); 78, 1396 (1997)

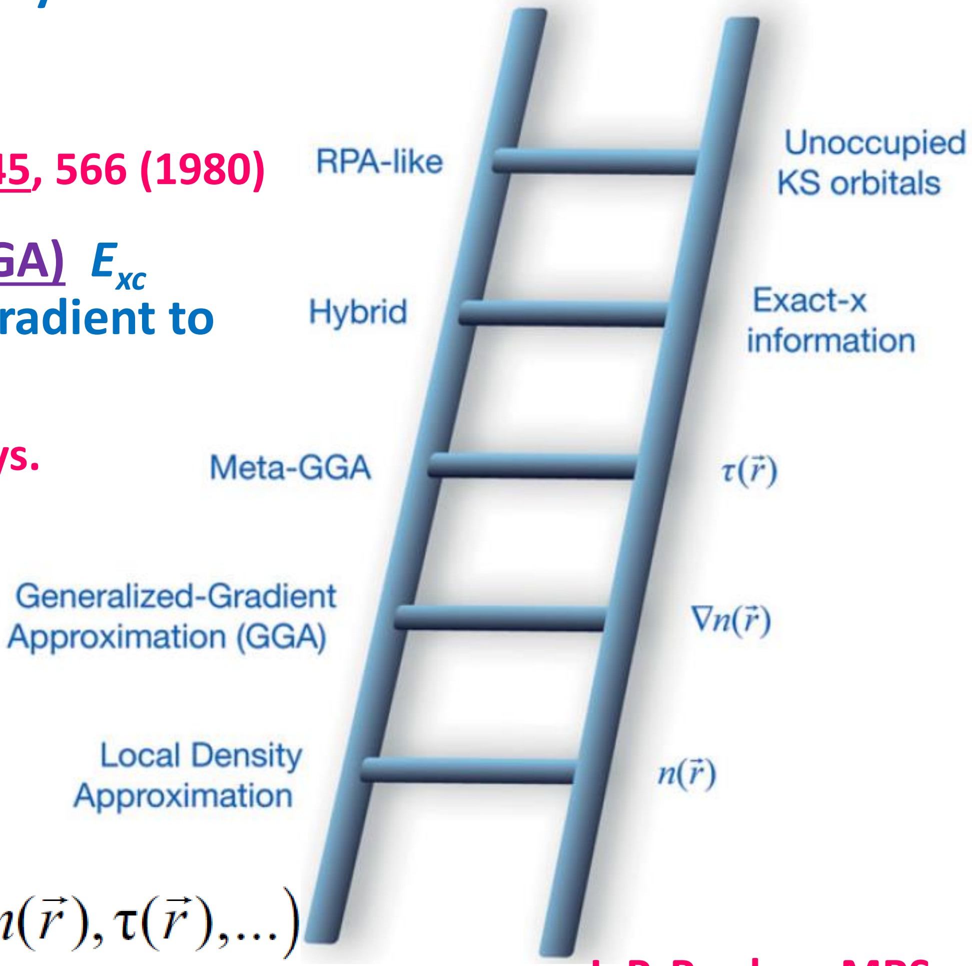
Meta-GGA E_{xc} also depends on the kinetic energy density (TPSS)

$$\tau(\vec{r})=\frac{1}{2}\sum_{\substack{\alpha\sigma\\ \varepsilon_{\alpha\sigma}<\mu}}\left|\nabla\psi_{\alpha\sigma}(\vec{r})\right|^2$$

$$E_{xc}^{approx}[n]=\int d^3r\, n(\vec{r})\,\varepsilon_{xc}^{approx}(n(\vec{r}),\nabla n(\vec{r}),\tau(\vec{r}),\ldots)$$

J. Tao , J.P. Perdew , V.N. Staroverov , G.E. Scuseria *Phys. Rev. Lett.* 91, 146401 (2003)

Perdew's ladder of DFT functionals



J. P. Perdew, MRS Bulletin 38, 743 (2013)

DFT Functionals: Hybrid Functionals

Hybrid Functionals A fraction,α, of exact (Fock) exchange is mixed with GGA exchange and correlation. PBE0 has 25% EXX

$$E_x^{HF} = -\frac{1}{2}\sum_{i,j}\iint \varphi_i^*(r_1)\varphi_j^*(r_1)\frac{1}{r_{12}}\varphi_i(r_2)\varphi_j(r_2)dr_1dr_2$$

C. Adamo and V. Barone, *J. Chem. Phys*. 110, 6158 (1999)

Range-Separated Hybrids The Coulomb potential is split into short-range and long-range parts

$$\frac{1}{r_{12}} = \frac{\mathrm{erfc}(\omega r_{12})}{r_{12}} + \frac{\mathrm{erf}(\omega r_{12})}{r_{12}}$$

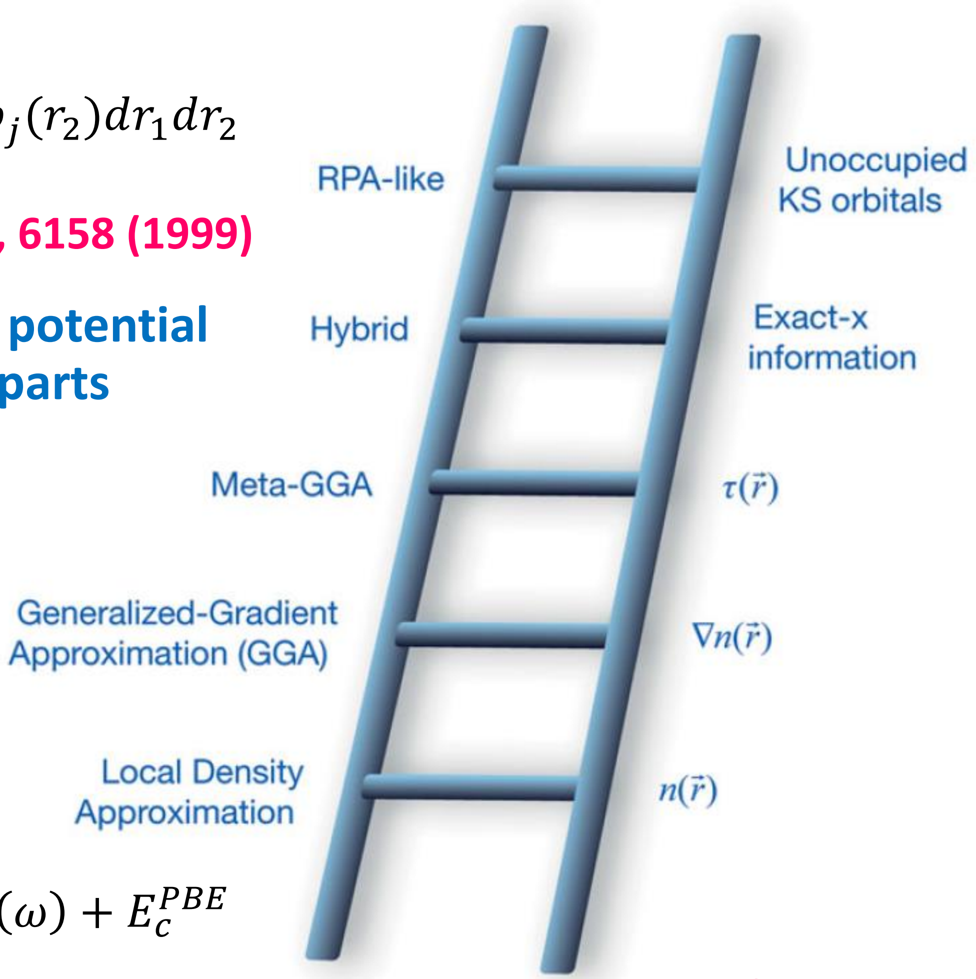
1/ω is a characteristic length scale for SR-LR transition

HSE reduces to PBE0 in the SR and to PBE in the LR (α=0.25; ω=0.11 Bohr^{-1}

$$E_{xc}^{HSE} = \alpha E_x^{HF,SR}(\omega) + (1-\alpha)E_x^{\omega PBR,LR}(\omega) + E_c^{PBE}$$

J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys*. 118, 8207 (2003); 124, 219906 (2006)

Perdew's ladder of DFT functionals

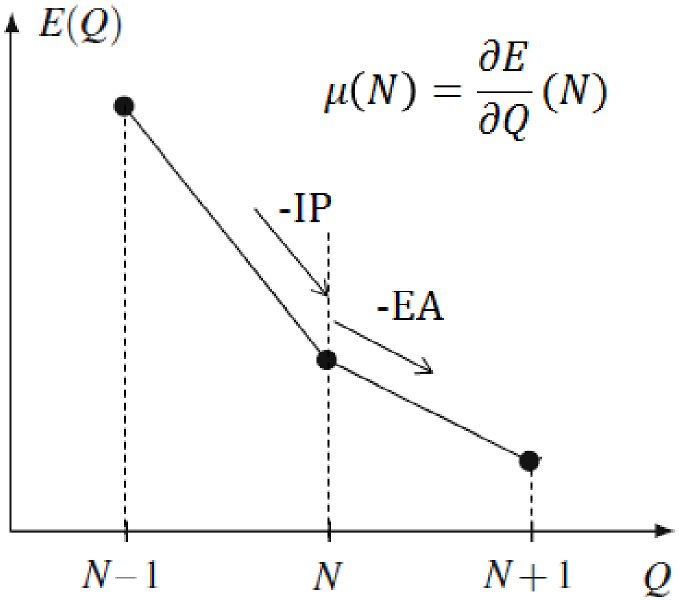


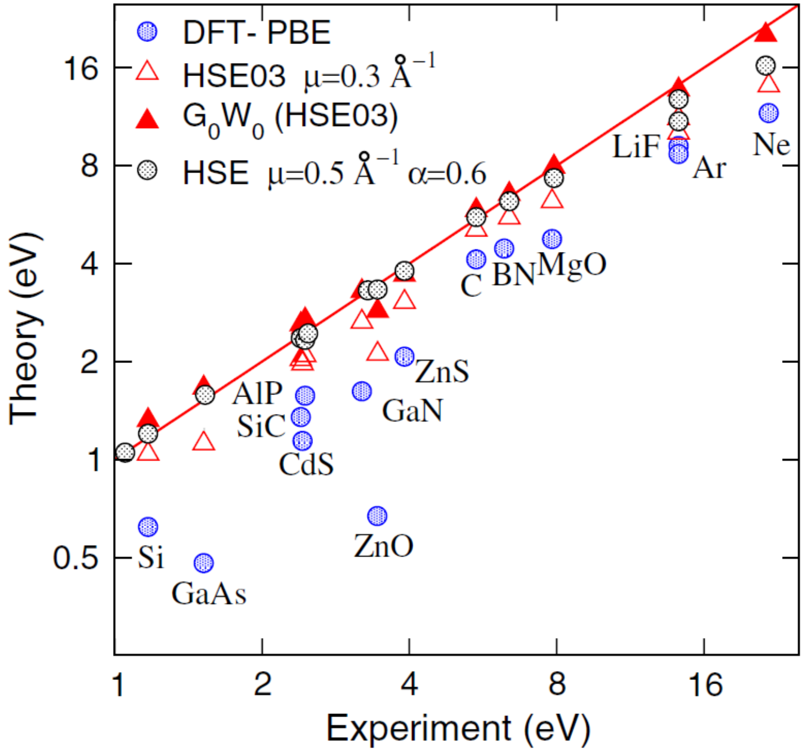
J. P. Perdew, MRS Bulletin 38, 743 (2013)

Pathologies of Semi-Local Functionals

The (lack of) Derivative Discontinuity: The chemical potential is supposed to jump discontinuously when going through an integer particle number

The Self-Interaction Error: Spurious Coulomb repulsion of an electron from itself due to incomplete cancellation of the self-interaction in the Hartree term by the approximate exchange term



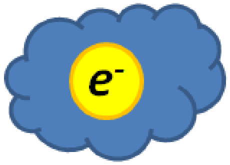


Effects: Destabilization of localized states and severe gap underestimation

Hybrid functionals mitigate (but not completely correct!) these deficiencies

The GW Approximation

The quasiparticle equation:



$$\left(-\tfrac{1}{2}\nabla^2 + V_{ion} + V_{Hartree} + \underset{\text{many-body}}{\overset{\text{self-energy}}{\Sigma(r,r',E_i^{QP})}}\right)\psi_i(r) = E_i^{QP}\psi_i(r)$$

The GW approximation (Hedin, 1965):

The **self-energy** is approximated by the first order term in a perturbative expansion in the screened Coulomb interaction

$$\Sigma \approx iGW$$

G_0W_0 (Hybertsen and Louie, 1986):

- Assume that the KS wave-function and eigenvalues are good approximations for the many-body wave-function and QP energies
- Calculate the QP energies non-self-consistently as perturbative corrections to the KS energies:

$$E_i^{G_0W_0} = \varepsilon_i^{KS} + \left\langle \varphi_i \middle| \Sigma^{G_0W_0} - V_{xc} \middle| \varphi_i \right\rangle$$

- Use KS orbitals and energies to evaluate G_0 and W_0

DFT in Practice: Common Basis Sets and Codes

To solve the Kohn-Sham eigenvalue equation in practice, it must be discretized in a basis set. Different DFT codes use different basis sets:

Plane-waves (PW) are the most convenient basis set for periodic systems: VASP, Quantum Espresso, ABINIT, CASTEP

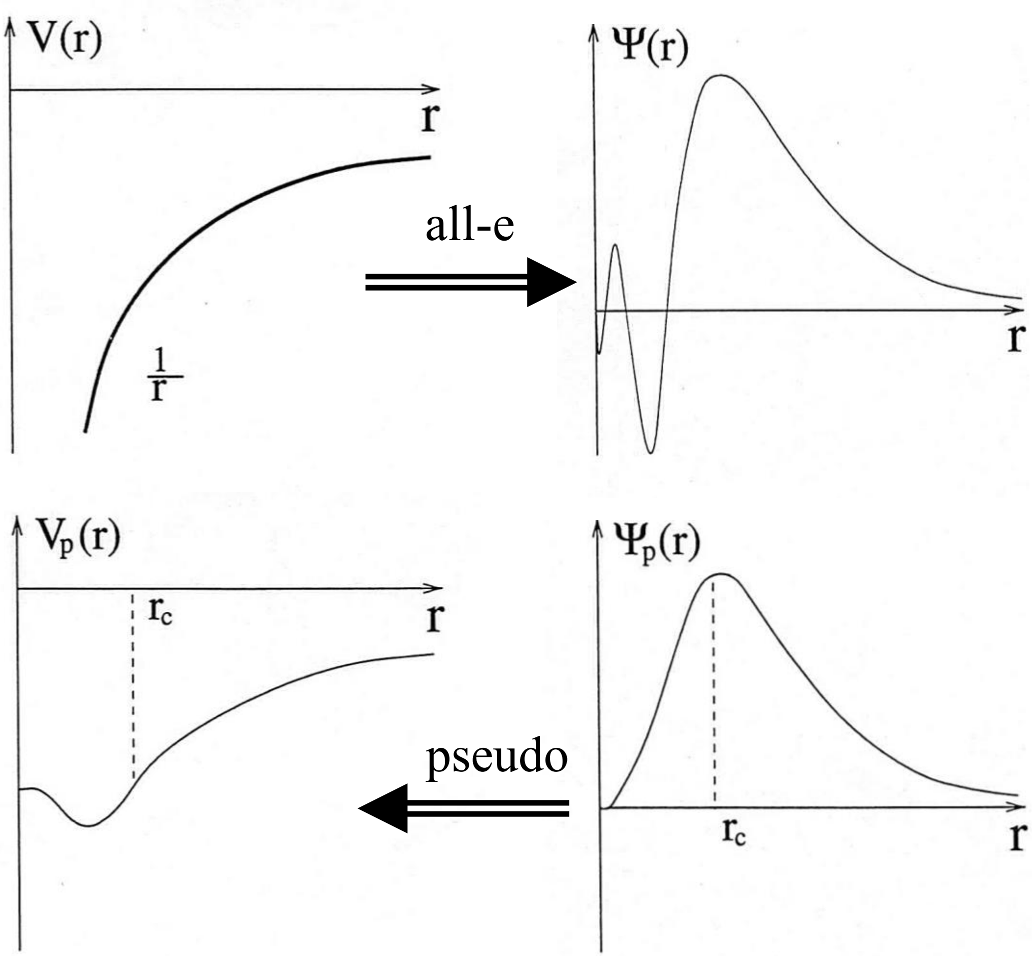
Other types of basis sets:
Real space: PARSEC, OCTOPUS
Wavelets: BigDFT, MADNESS
Gaussian orbitals (GTO): NWChem, Q-Chem, Gaussian, CRYSTAL
Slater orbitals (STO): ADF
Numeric atom-centered orbitals (NAO): FHI-aims, SIESTA CONQUEST
Full potential linearized augmented plane-waves (FP-LAPW): EXCITING, FLEUR, ELK, WIEN2k

See also:
https://en.wikipedia.org/wiki/List_of_quantum_chemistry_and_solid-state_physics_software

DFT in Practice: Pseudo Potentials

Core electrons do not contribute significantly to chemical bonding and physical phenomena of interest (except for X-ray spectroscopies) but do contribute high frequency terms in the wave-function that are numerically difficult to deal with

The wave-function in the core region is replaced by a smooth function and the 1/r potential by a slowly-varying pseudo-potential



Common types of pseudo-potentials:

- Norm-conserving
- Ultra-soft
- Projector augmented waves (PAW)

Keeping Supercomputers Busy…

Hopper (#34)
Cray XE6
153,216 cores
1.28 petaflops

Edison (#18)
Cray XC30
133,824 cores
2.77 petaflops

Mira (#5)
BlueGene/Q
786,432 cores
8.6 petaflops

The computational cost of quantum mechanical simulations increases with the accuracy of the method and with the system's size and complexity

Configuration space exploration may require running *thousands* of trial structures

New at Tulane:
Cypress (#271)
Dell cluster
2,480 Intel Ivy Bridge+ 15,128 Xeon Phi cores
0.7 petaflops

Computational Cost of Different Methods (FHI-aims)

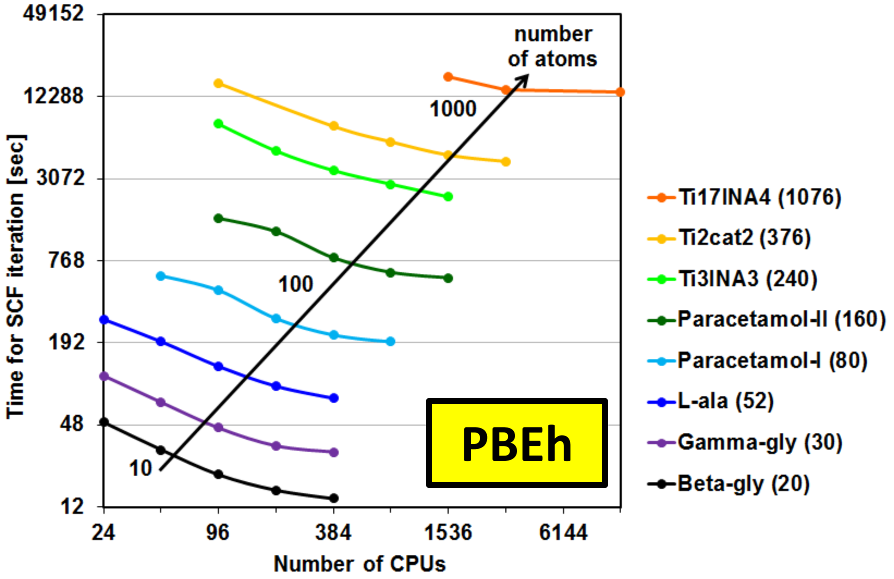
Local and semi-local **functionals -> low computational cost, good scaling**

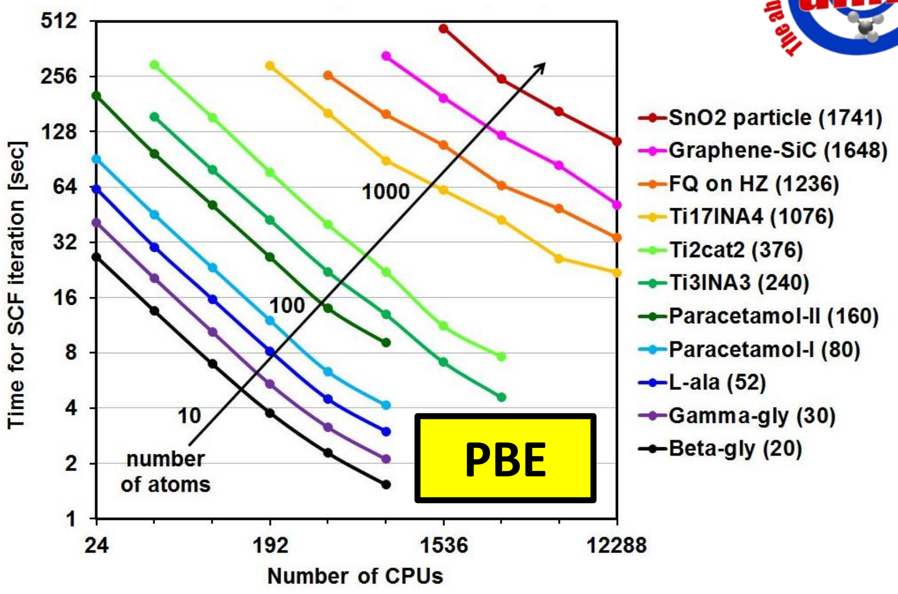
Non-local **functional -> better accuracy, higher computational cost, worse scaling**

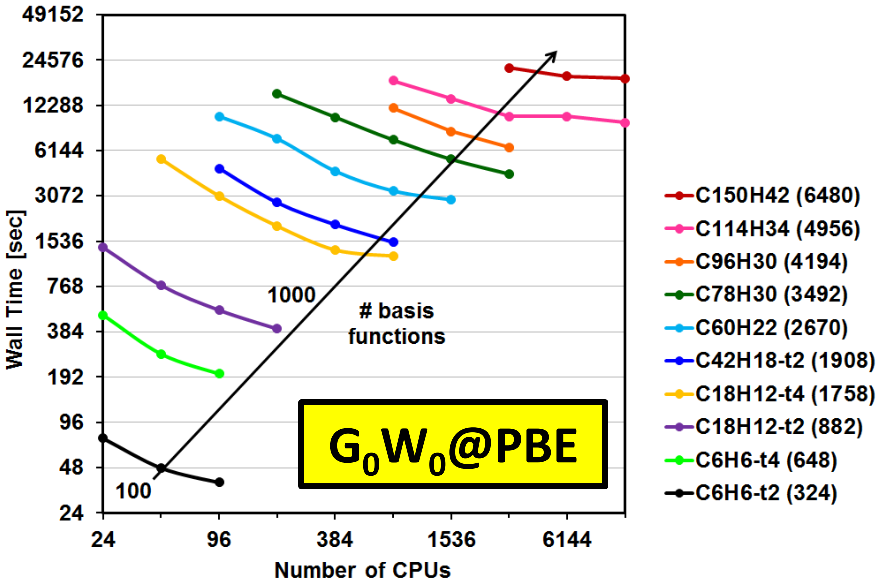
Scaling of semi-local DFT: O(N^3) -> O(N)

Hybrid DFT: O(N^4) -> O(N)*large prefactor

G_0W_0: O(N^4) -> O(N^3) (post SCF)





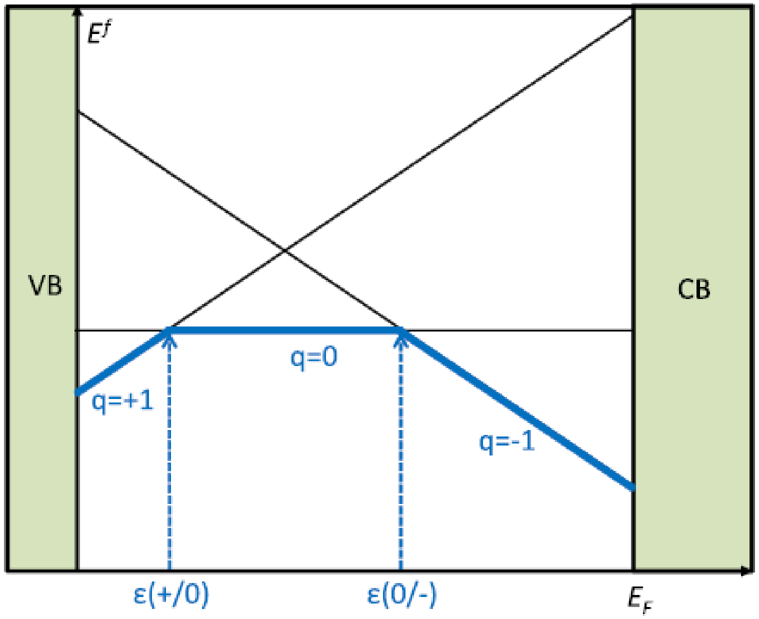


Applying DFT to Defects in Semiconductors

Formation energies:

Neutral defect: $$E^f[X^0] = E_{\text{tot}}[X^0] - E_{\text{tot}}[\text{bulk}] - \sum_i n_i \mu_i$$

Charged defect: $$E^f[X^q] = E_{\text{tot}}[X^q] - E_{\text{tot}}[\text{bulk}] - \sum_i n_i \mu_i + qE_F + E_{\text{corr}}$$



The chemical potential:

Determined by the conditions (T,P) of the experiment and used to simulate different conditions

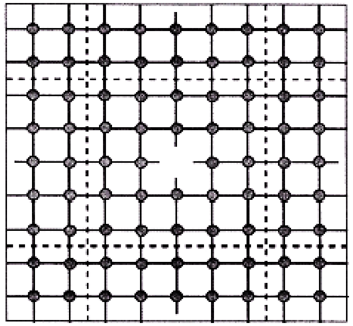
A consistent choice of reference must be made, either to the total energy of the elemental phases at 0K or at STP

Chemical potentials are bound by the existence or appearance of secondary phases

Freysoldt *et al.*, *Rev. Mod. Phys.* 86, 253 (2014)

Applying DFT to Defects in Semiconductors

The supercell approximation:



The defect is placed in a large simulation cell with periodic boundary conditions

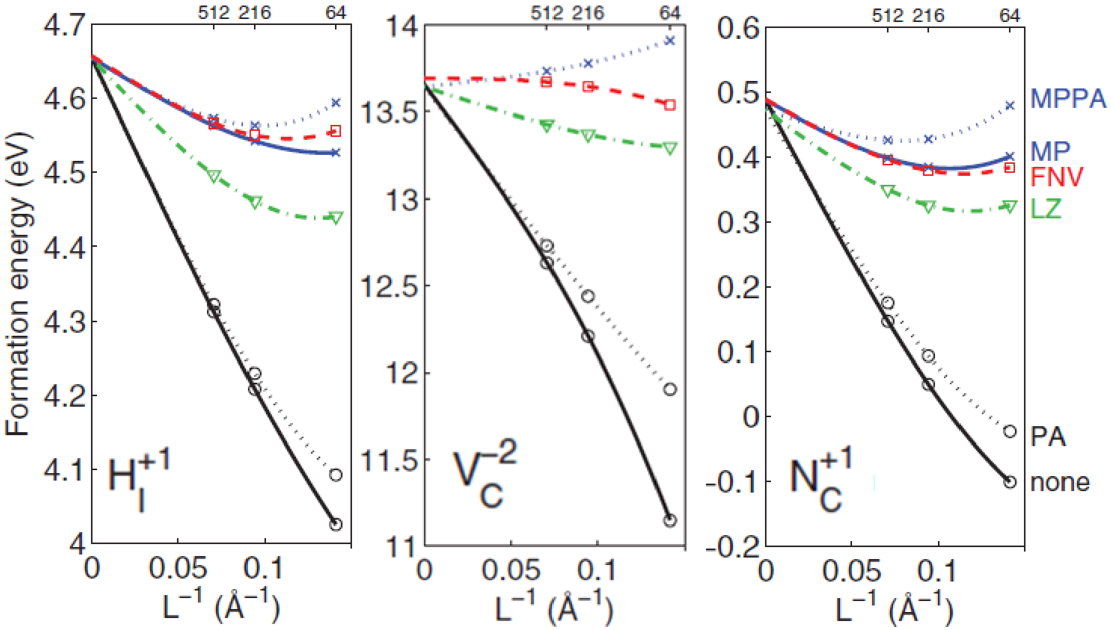
Higher effective concentration of defects

Interactions between periodic replicas may broaden the defect state

For charged defects a compensating background charge is added

The slow decay of the Coulomb potential leads to spurious interactions

Defects in diamond



Various correction schemes:

Makov and Payne (MP)

Freysoldt, Neugebauer, and Van de Walle (FNV)

Lany and Zunger (LZ)

Potential alignment (PA)

H. P. Komsa, T. Rantala, & A. Pasquarello *PRB* 86, 045112 (2012)

Applying DFT to Defects in Semiconductors

Comprehensive review: Freysoldt *et al.*, *Rev. Mod. Phys.* 86, 253 (2014)

Things to worry about:

- ✗ (In)accuracy of the exchange-correlation functional
- ✗ Supercell artifacts

Best practices:

- ✓ Start by reproducing known results
- ✓ Check carefully the sensitivity of the results to the parameters of the calculations (DFT functional, supercell size, etc.)
- ✓ Cross-validate using different methods
- ✓ Qualitative trends are more reliable than absolute numbers

Case Study: Designing a Shallow Donor in Diamond

UT-Austin, 2010

Jonathan E. Moussa, Noa Marom, Na Sai, James R. Chelikowsky

PRL 108, 226404 (2012)

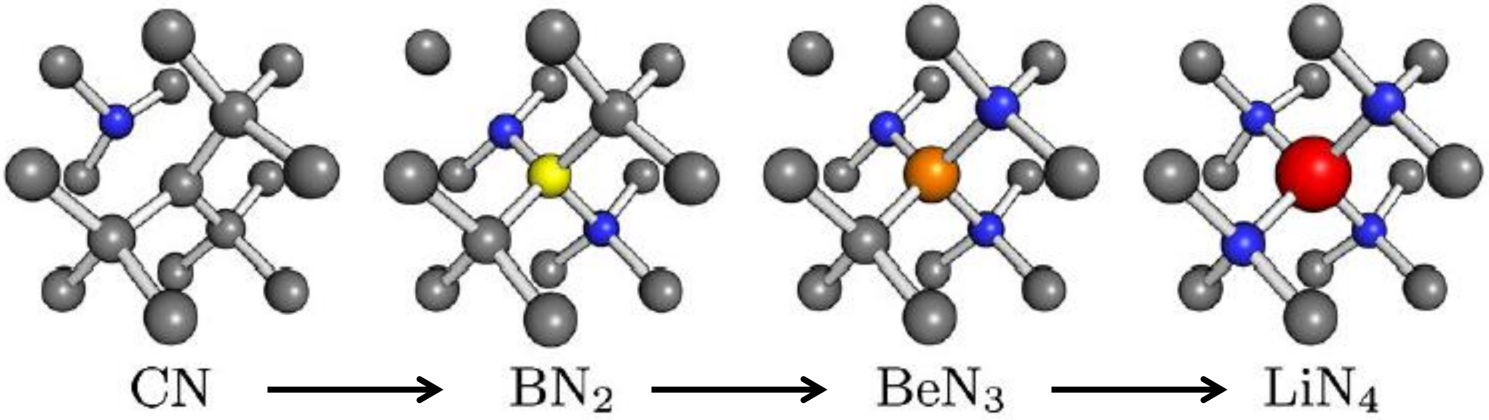
Motivation:

- ✓ Diamond has desirable properties for high-power, high-temperature electronics
- ✓ Boron is a good *p*-type dopant
- ✗ The lack of appropriate *n*-type dopant limits its applications

P. W. May "A New Diamond Age?" *Science* 319, 1490 (2008)

Case Study: Designing a Shallow Donor in Diamond

Shallow donor proposals:



The broken C-N bond near a substitutional N impurity forms a deep, localized donor state

Preserving the bond may create a shallower and more delocalized donor

A series of XN_n impurity complexes is generated by reducing the valence of the central atom and compensating with neighboring N atoms

For LiN_4 there are no broken bonds at the equilibrium geometry

Is it shallow? Can it be synthesized?

J. E. Moussa, N. Marom, N. Sai, J. R. Chelikowsky *PRL* 108, 226404 (2012)

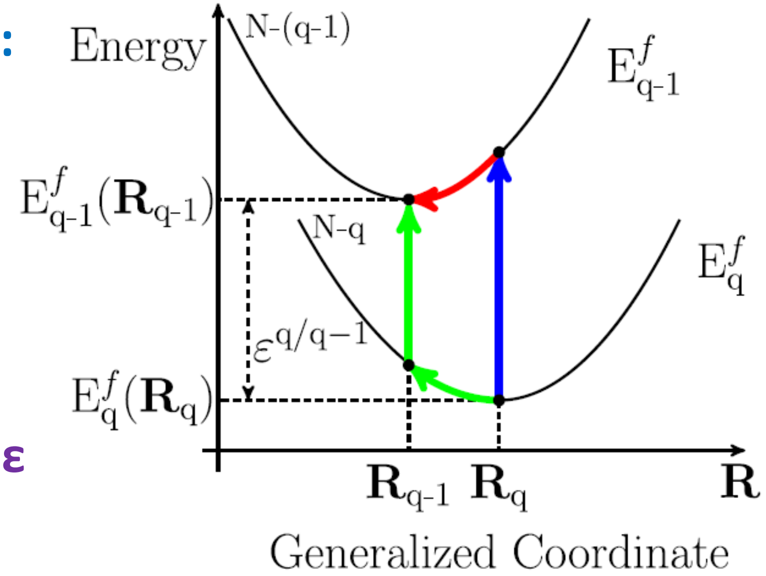
Case Study: Designing a Shallow Donor in Diamond

Method:

Decomposition of the donor activation energy:

Relaxation energy (the energy difference between the charged and neutral geometries) calculated with a *total energy method:* PBE

Vertical ionization energy (at the fixed geometry of the ionized donor) calculated with an *accurate quasi-particle method:* PBE0-ε and *corrected for finite size effects*



M. Jain, J. R. Chelikowsky, S.G. Louie *PRL* 107, 216803 (2011)

$$\Delta_D = E_c + E^+_{\rm tot}(\mathbf{R}^+_D) - E^0_{\rm tot}(\mathbf{R}^0_D)$$

$$= \underbrace{[E_c - E_D(\mathbf{R}^+_D)]}_{\Delta_D^{\rm ionize}} + \underbrace{[E^0_{\rm tot}(\mathbf{R}^+_D) - E^0_{\rm tot}(\mathbf{R}^0_D)]}_{\Delta_D^{\rm relax}}$$

J. E. Moussa, N. Marom, N. Sai, J. R. Chelikowsky *PRL* 108, 226404 (2012)

Case Study: Designing a Shallow Donor in Diamond

Step 1: Pick a reliable method

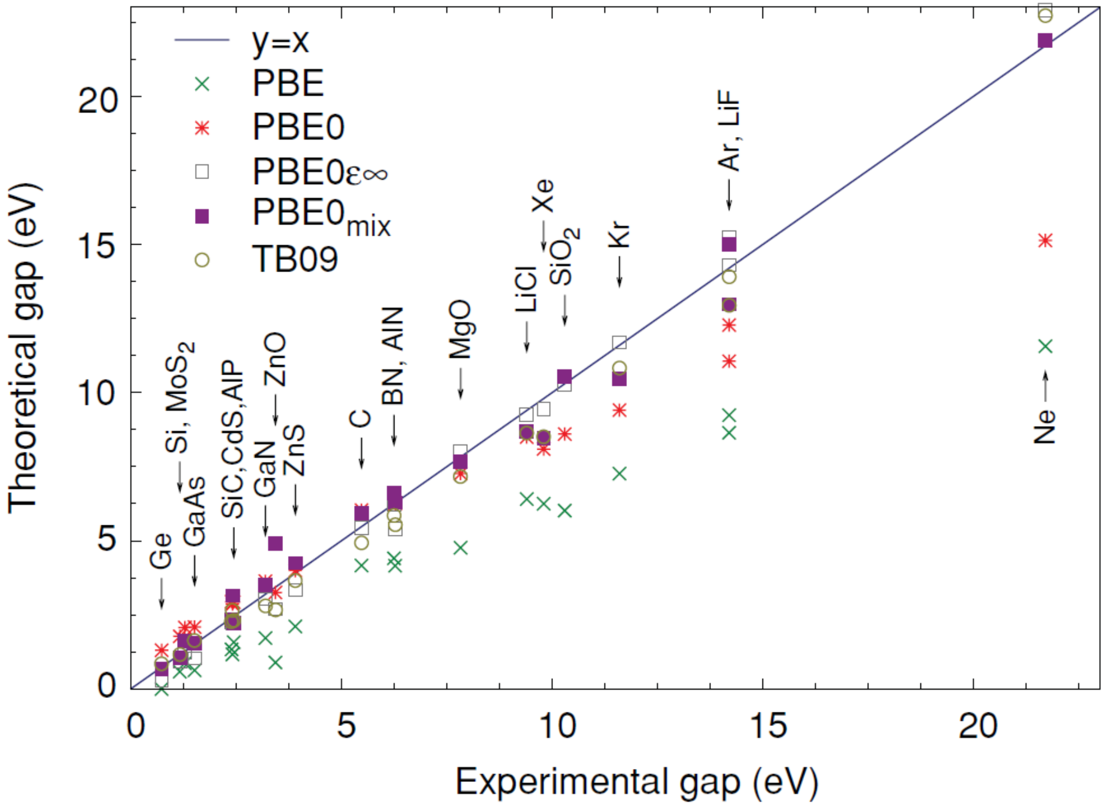
PBE0-ε:

A PBE-based hybrid functional with a system-dependent fraction, α, of exact (Fock) exchange, determined by the dielectric constant:

α = 1/ε

Marquez et al. *PRB* 83, 035119 (2011)

For diamond:
ε = 5.7; α= 0.18

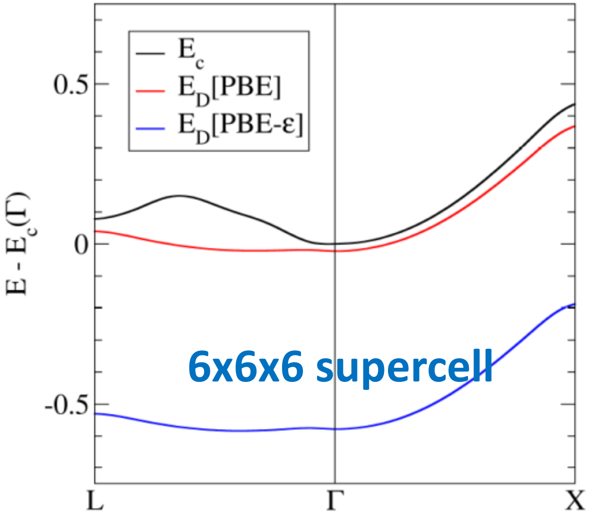


J. E. Moussa, N. Marom, N. Sai, J. R. Chelikowsky *PRL* 108, 226404 (2012)

Case Study: Designing a Shallow Donor in Diamond

Step 2: Finite size correction

Defect band dispersion model:



6x6x6 supercell

Interactions between periodic replicas cause broadening of the defect band

Δ_D^{ionize} was calculated using supercells of 5x5x5 to 8x8x8 diamond unit cells

The impurity band becomes shallower and narrower with size

Define: $$\Delta_D^{\text{ionize}} \approx E_c(\Gamma) - [(1-x)E_D(\Gamma) + xE_D(X)]$$

A least square fit is performed with x as a free parameter to minimize the size dependence of Δ_D^{ionize} around an asymptotic value

This gives Δ_D^{ionize} =0.27 eV (x = 0.74)

J. E. Moussa, N. Marom, N. Sai, J. R. Chelikowsky *PRL* 108, 226404 (2012)

Case Study: Designing a Shallow Donor in Diamond

Step 3: Cross-validation

The marker method:

Activation energies are calculated based on PBE total energy differences and referenced to an experimentally known "marker" impurity

$$\Delta_i = \underbrace{\Delta_0}_{\text{fit to experiment}} - [E_{N-1} - E_N]_{\text{defect } 0} + [E_{N-1} - E_N]_{\text{defect } i}$$

A. Resende *et al.*, *Phys. Rev. Lett*. 82, 2111 (1999)

The applicability of the marker method is limited to cases with:

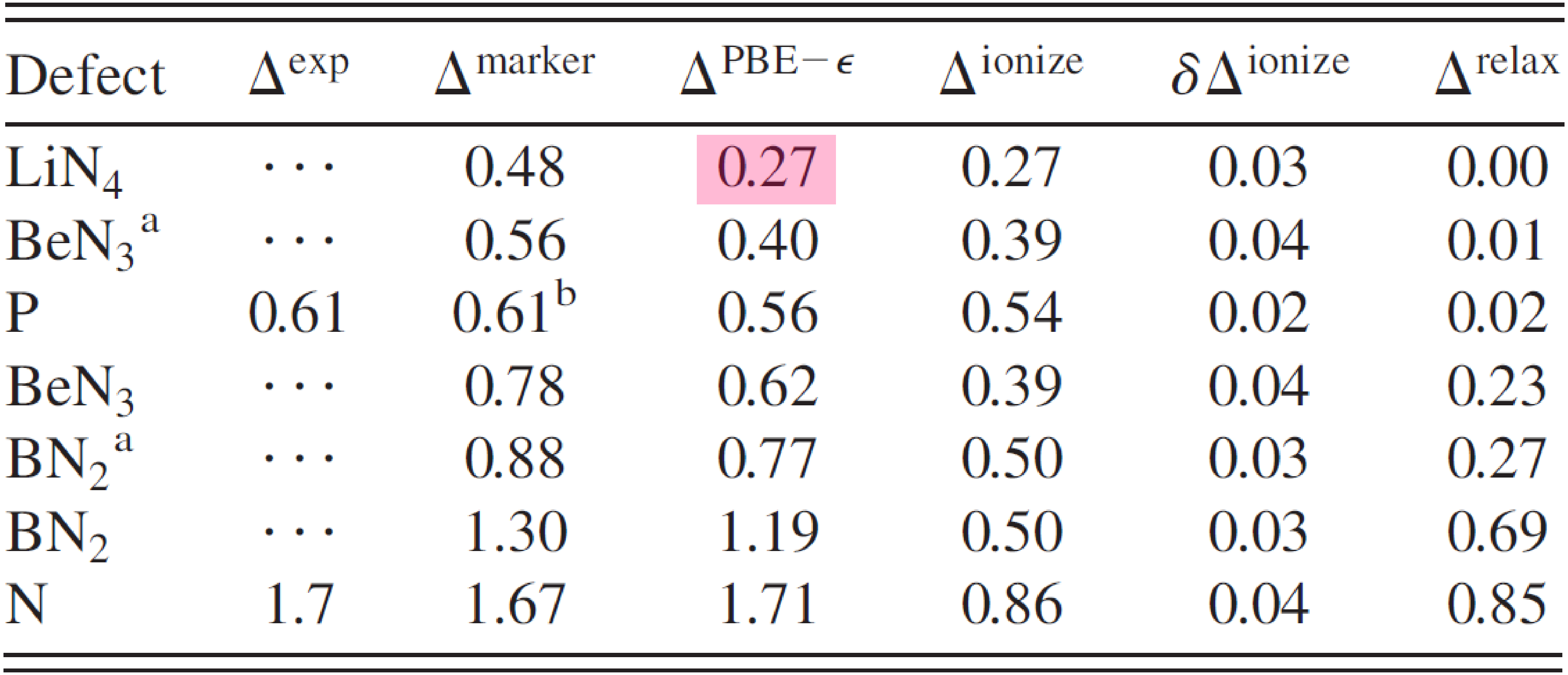
***same* simulation conditions**
***same* material environment**
***same* defect type**
***same* charge state**

Activation energies obtained with the marker method are overestimated due to the self-interaction (delocalization) error in PBE

J. E. Moussa, N. Marom, N. Sai, J. R. Chelikowsky *PRL* 108, 226404 (2012)

Case Study: Designing a Shallow Donor in Diamond

LiN_4 is a promising shallow donor in diamond



Defect	Δ^{exp}	Δ^{marker}	$\Delta^{\mathrm{PBE}-\epsilon}$	Δ^{ionize}	$\delta\Delta^{\mathrm{ionize}}$	Δ^{relax}
LiN_4	···	0.48	0.27	0.27	0.03	0.00
BeN_3[a]	···	0.56	0.40	0.39	0.04	0.01
P	0.61	0.61[b]	0.56	0.54	0.02	0.02
BeN_3	···	0.78	0.62	0.39	0.04	0.23
BN_2[a]	···	0.88	0.77	0.50	0.03	0.27
BN_2	···	1.30	1.19	0.50	0.03	0.69
N	1.7	1.67	1.71	0.86	0.04	0.85

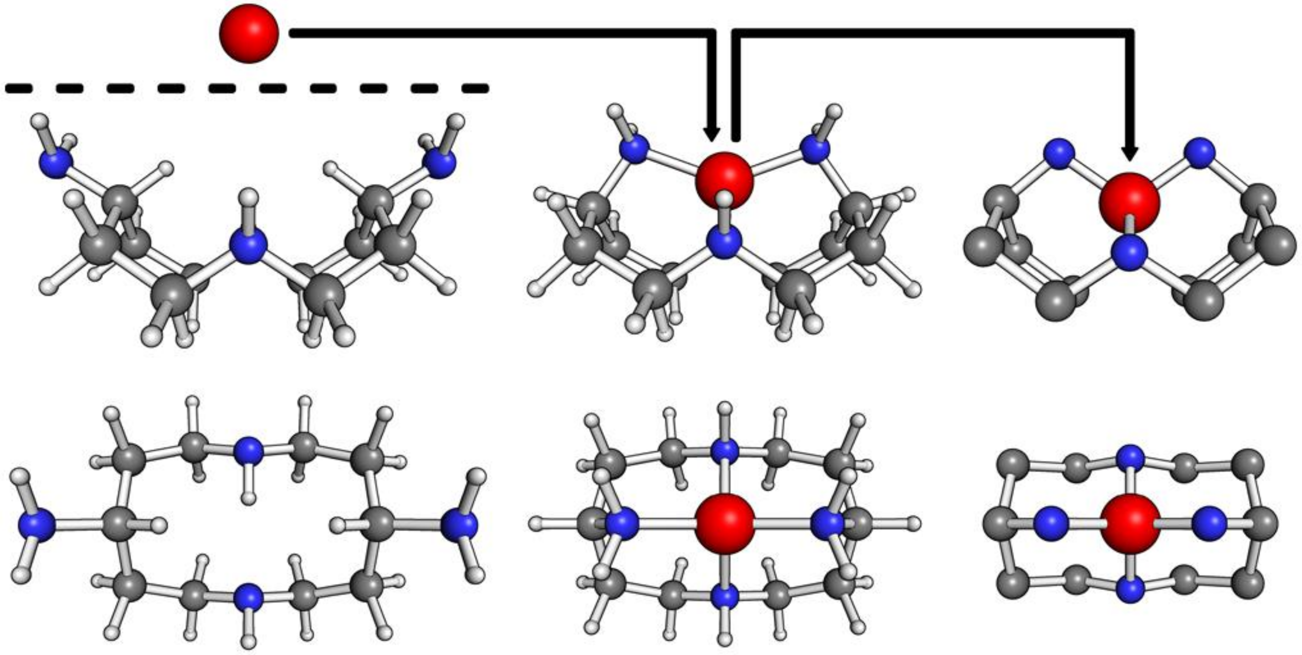
J. E. Moussa, N. Marom, N. Sai, J. R. Chelikowsky *PRL* 108, 226404 (2012)

Case Study: Designing a Shallow Donor in Diamond

Possible CVD precursor:

1,7-diazacyclododecane-4,10-diamine can strongly bind a Li atom

The Li atom is not bound to the B-center in diamond but kinetically stabilized by a high energy barrier



E=0.00 eV

E= -1.59 eV

E= 0.91 eV

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