SAND2015-1354C

Designing shallow donors in diamond

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U.S. DEPARTMENT OF ENERGY

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Collaborators

1. Shallow donors *in* diamond [PRL **108**, 226404 (2012)]

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UT Austin

Noa Marom
Tulane University

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UT Austin

2. Shallow donors (in vacuum) *made of* diamond

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Sandia National Labs

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Sandia National Labs

Motivation

Diamond is useful for high-power / high-temperature electronics,

semiconductor figures of merit

	V·*ω* limit	*T* limit	*R* limit	*C* limit
Si	1	1	1	1
GaAs	2	0.4	10	10
α-SiC	20	4	100	10
C	30	40	7000	400

[B. J. Baliga, IEEE Electron Device Lett. **10**, 455 (1989)]

… but you need both *p*-type & *n*-type for many applications.

B_s P_s?

[“*The New Diamond Age?*”, Paul W. May, Science **319**, 1490 (2008)]

Shallow impurities are a challenging computational problem,

$$\frac{\text{effective Bohr radius}}{\text{lattice constant}} = 1.8 \text{ in diamond} \qquad (= 4.4 \text{ in Si})$$

Effective mass model

$$\left[-\frac{\nabla^2}{2m^*} - \frac{1}{\epsilon r}\right]\psi(\mathbf{r}) = -\Delta\psi(\mathbf{r})$$

(Hartree atomic units)

$$|\psi(\mathbf{r})|^2 \propto e^{-2r/R}$$

$$R = \frac{\epsilon}{m^*}$$

$$\Delta = \frac{m^*}{2\epsilon^2}$$

In Si,

R = 24 Å
Δ = 0.025 eV
Δ(P_s) = 0.045 eV

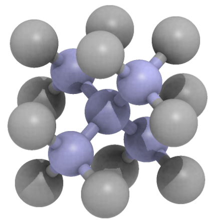
In diamond,

R = 6.3 Å
Δ = 0.20 eV
Δ(P_s) = 0.61 eV

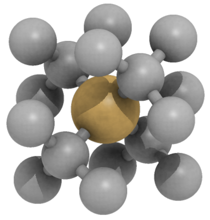
+ anisotropy + multi-band + multi-valley + non-quadratic dispersion + central-cell + …

effective mass modeling @ Sandia: **W37.00008** **W37.00009** **W37.00010** (Thursday)

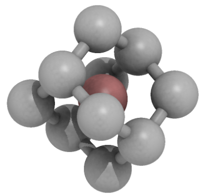
Shallow donor proposals



$(\frac{4}{5}C+\frac{1}{5}N)_5$



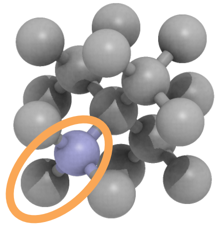
P_s

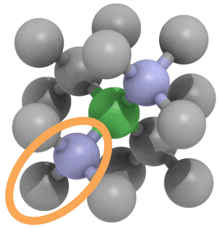


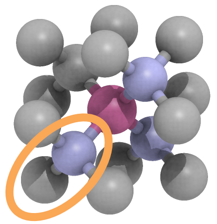
Li_i

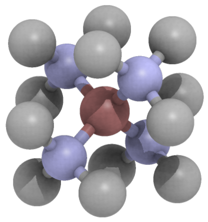
Idealized donor (alchemy)

Monoatomic donors (strained)



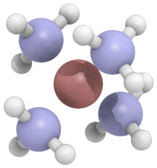






XH_n or N → BN_2 → BeN_3 → LiN_4

Donor complexes (complicated defect chemistry)



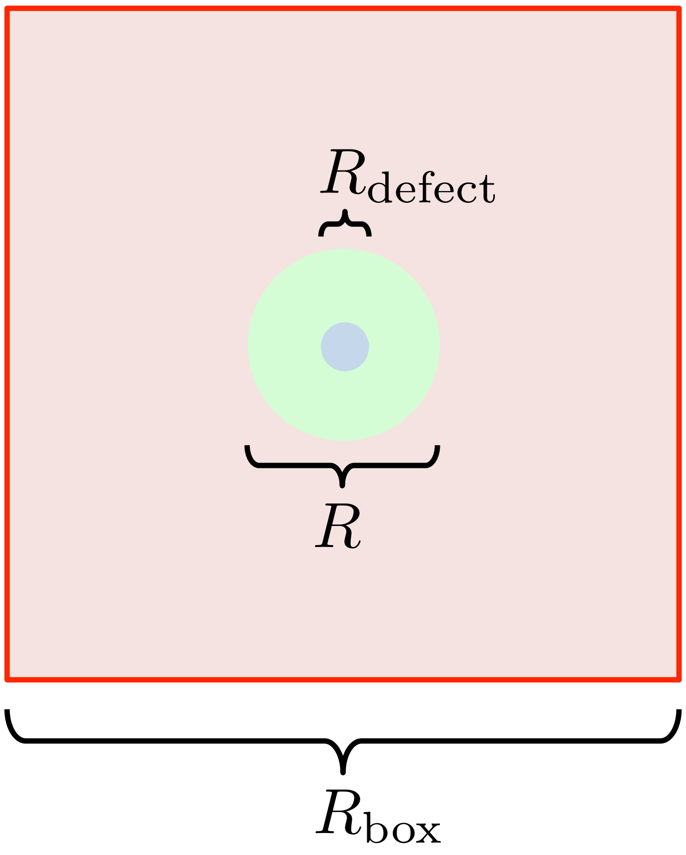
$Li(NH_3)_4$

metallic

High natural abundance of N in diamond!

Key questions: Is it shallow? & Can we make it?

Methodology (ideal)



$$R_{\mathrm{box}} \gg R > R_{\mathrm{defect}}$$

Primary DFT observables:

$$E_{N\pm1} - E_N$$

$$\rho_{N\pm1}(\mathbf{r}) - \rho_N(\mathbf{r})$$

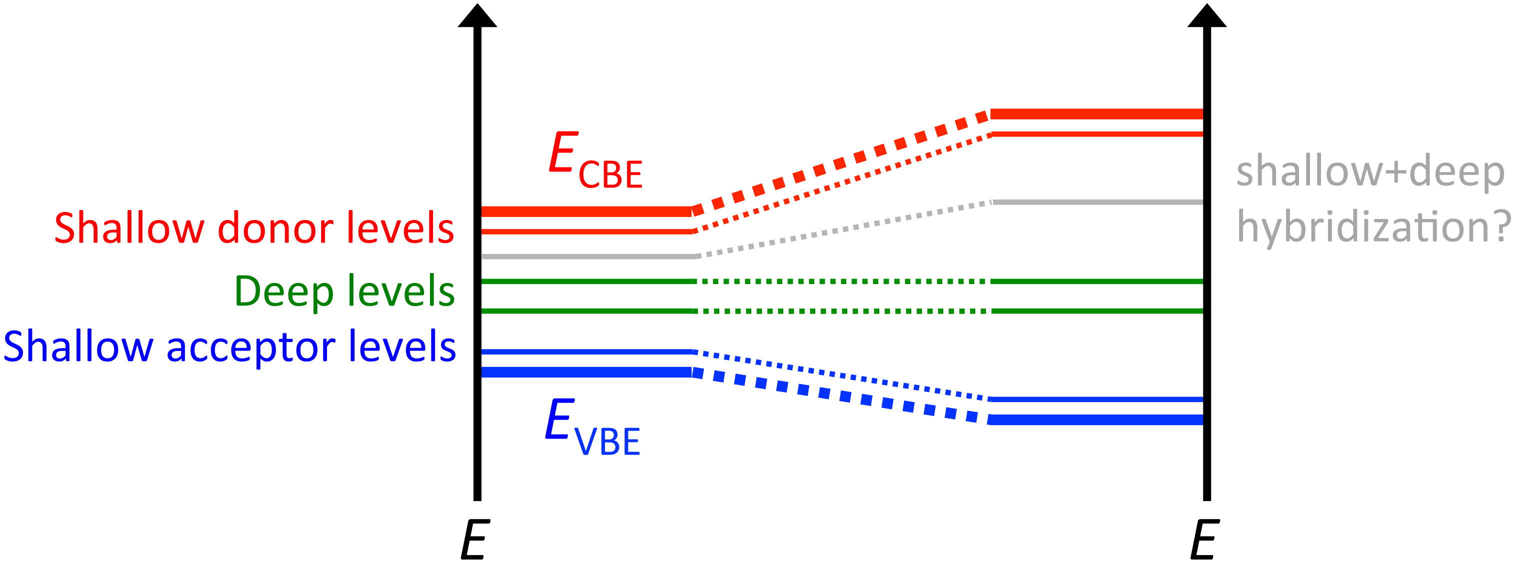
relative energetics
sufficiently accurate
& free of pathologies

Simple donor level recipe:

$$\begin{aligned}\Delta =& [E_{N+1} - E_N]_{\mathrm{pristine}} \\ &+ [E_{N-1} - E_N]_{\mathrm{defect}}\end{aligned}$$

a big box & a good functional

Band gap problems



Semilocal DFT functionals underestimate band gaps:

$$E_{\mathrm{CBE}} - E_{\mathrm{VBE}} \approx [E_{N+1} - 2E_N + E_{N-1}]_{\mathrm{pristine}}$$

Systematic errors typically preserve relative energies between like defects.

silver lining? reliable? predictive?

Kohn-Sham energy levels

vs.

quasiparticle energy levels

Methodology (marker)

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

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

Limited applicability:

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

More sophisticated methods (e.g. Makov-Payne, local moment counter-charge) separate band alignment and electrostatic corrections for defects with charge *Q*.

$\Delta \propto Q$

Kohn-Sham reference
empirical reference
…

$\Delta \propto Q^2$

Jellium counter-charge & charge-in-Jellium model
Gaussian counter-charge & dielectric cavity model
…

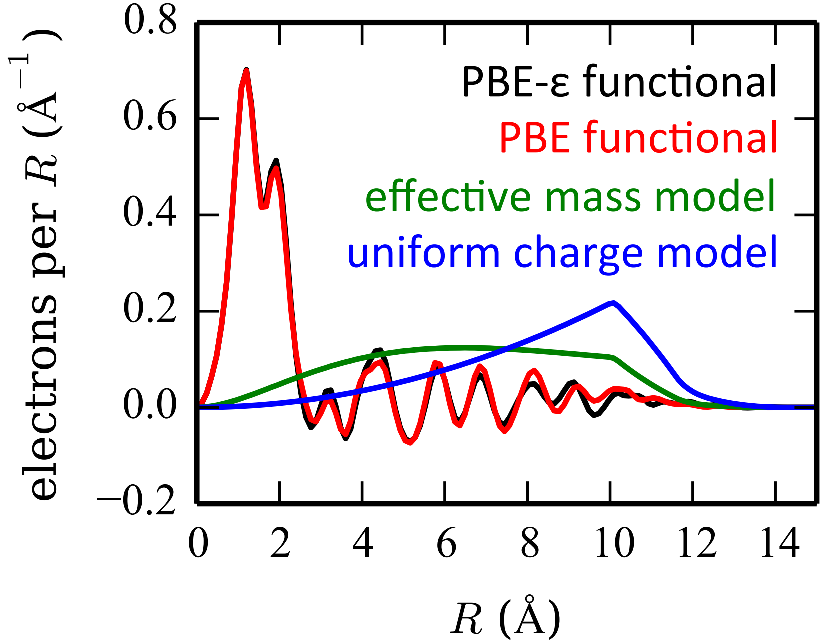
Self-interaction problems

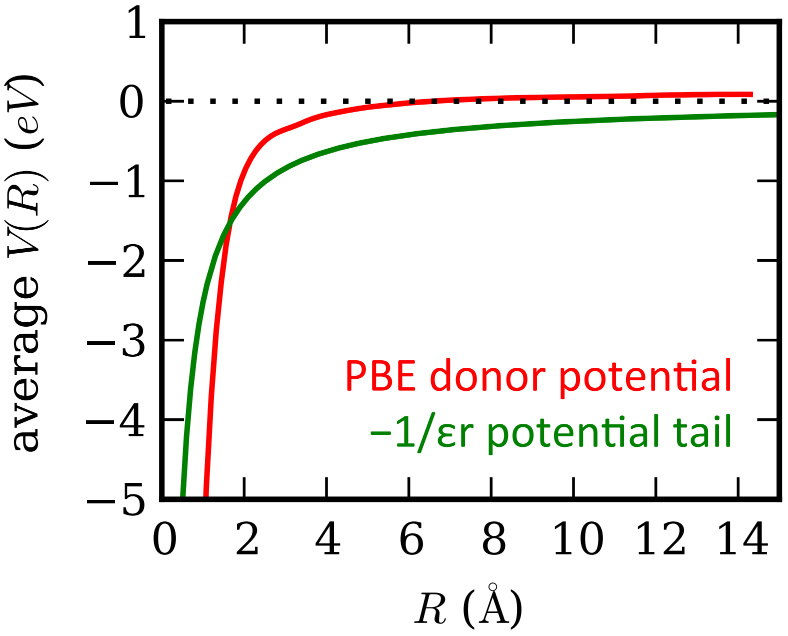
For shallow donors, large R_{box}, and semilocal DFT, indications of

$$\Delta = [E_{N+1} - E_N]_{\text{pristine}} + [E_{N-1} - E_N]_{\text{defect}} \approx 0$$

Where is the donor electron?

$$\rho_{\text{LiN}_4}(\text{r}) - \rho_{V\text{N}_4}(\text{r})$$





No asymptotic donor binding!

Defect-centered Wigner-Seitz cell of 8^3 supercell, barely resolving individual donors

Methodology (PBE-ε)

1. PBE0 with hybrid fraction 1/ε decently approximates quasiparticle energies

0.18 in PBE-ε vs. 0.25 in PBE0 for diamond

[M. A. L. Marques *et al.*, Phys. Rev. B **83**, 035119 (2011)]

2. Separate adiabatic excitations into vertical excitations and relaxations:

$$\Delta = \underbrace{[E_{N+1} - E_N]_{\text{pristine}} + [E^{+}_{N-1} - E^{+}_{N}]_{\text{defect}}}_{\text{Identify PBE-ε Kohn-Sham energy levels}} + \underbrace{[E^{+}_{N} - E^{0}_{N}]_{\text{defect}}}_{\text{Total energy calculations}}$$

[M. Hedström *et al.*, Phys. Rev. Lett. **97**, 226401 (2006)]

3. Finite-size corrections with defect band dispersion model (Wannier-inspired)

Why should this work? Good asymptotic behavior:

$$\psi_{\text{donor}}(\mathrm{r}) \quad \text{sees} \quad \hat{H}_{\text{qp}} + \hat{H}_{\text{cc}} - \frac{1}{\epsilon r}$$

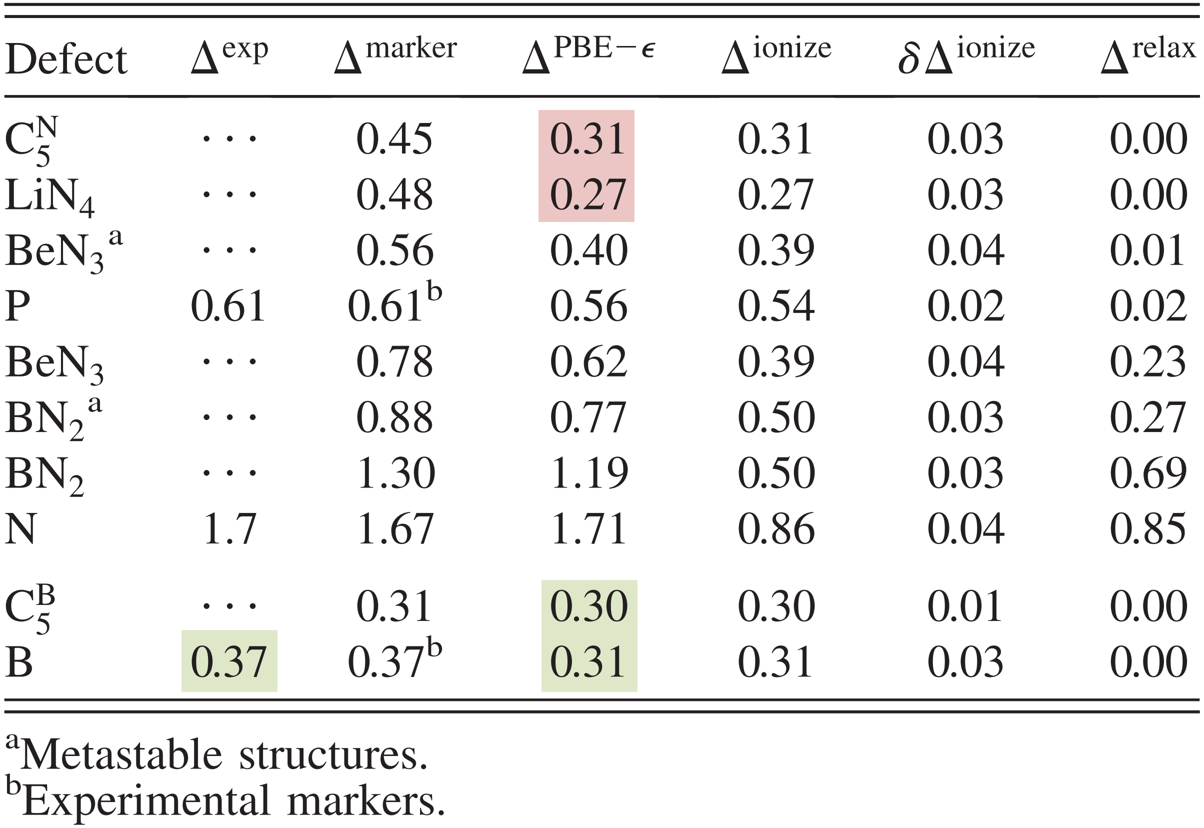
Numerical results

donors

≈0.20 eV

acceptors

≈0.45 eV



Defect	Δ^{exp}	Δ^{marker}	$\Delta^{\text{PBE}-\epsilon}$	Δ^{ionize}	$\delta\Delta^{\text{ionize}}$	Δ^{relax}
C_5^N	⋯	0.45	0.31	0.31	0.03	0.00
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
C_5^B	⋯	0.31	0.30	0.30	0.01	0.00
B	0.37	0.37[b]	0.31	0.31	0.03	0.00

[a] Metastable structures.
[b] Experimental markers.

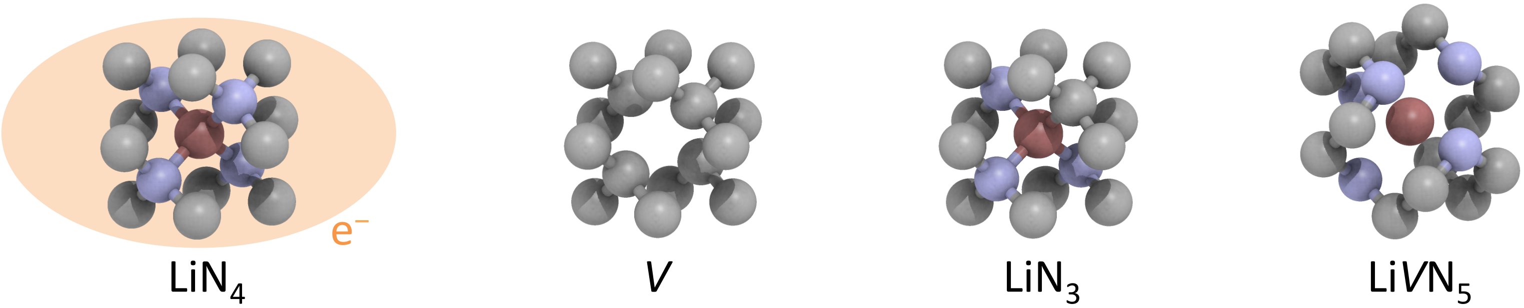
VASP calculation details: PBE total energies w/ 6^3 supercell & 2^3 BZ sampling
PBE-ε energy level extrapolation w/ 5^3, 6^3, 7^3, & 8^3 supercells
& simple model of inter-donor hopping decay

Marker results look reasonable even with underlying asymptotic problems.

Synthesis? (equilibrium)

Thermodynamic stability tests:

1. Enumerate competing defect structures:



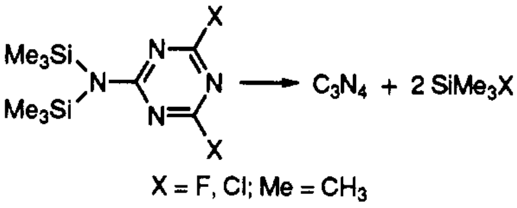
2. Search for destabilizing reactions:

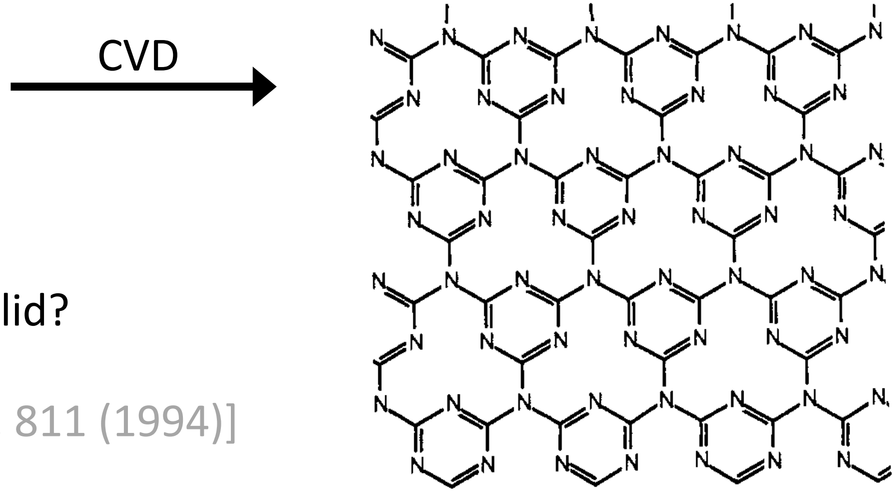
$2\ LiN_4 + V \longrightarrow LiN_3 + LiVN_5$ (favored by >2.5 eV)

3. (if we haven't failed) Calculate equilibrium distribution of defect / donor populations vs. composition / *P* / *T*

Synthesis? (nonequilibrium)

1. CVD-grown materials can retain precursor structure:

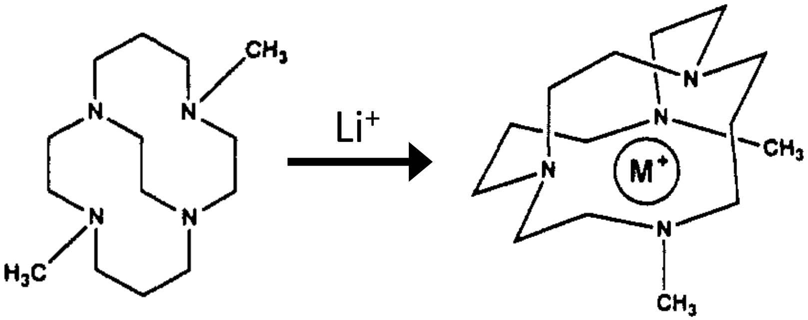




How crystalline is the solid?

[Kouvetakis *et al.*, Chem. Mater. **6**, 811 (1994)]

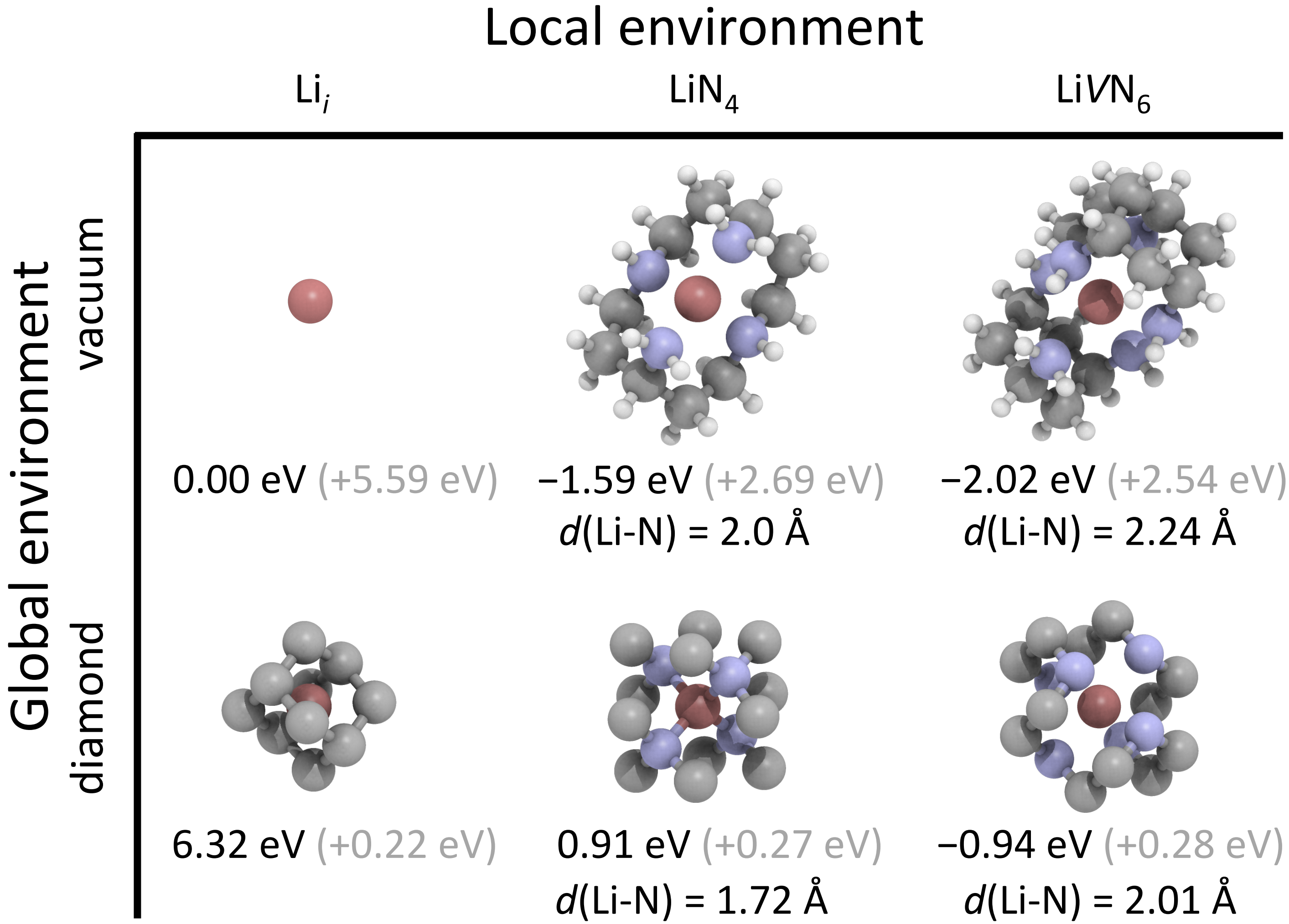
2. LiN$_4$ can be synthesized within an organic molecule:



Molecule selectively binds Li$^+$

[Weisman *et al.*, JACS **112**, 8604 (1990)]

Donor precursors



Local environment

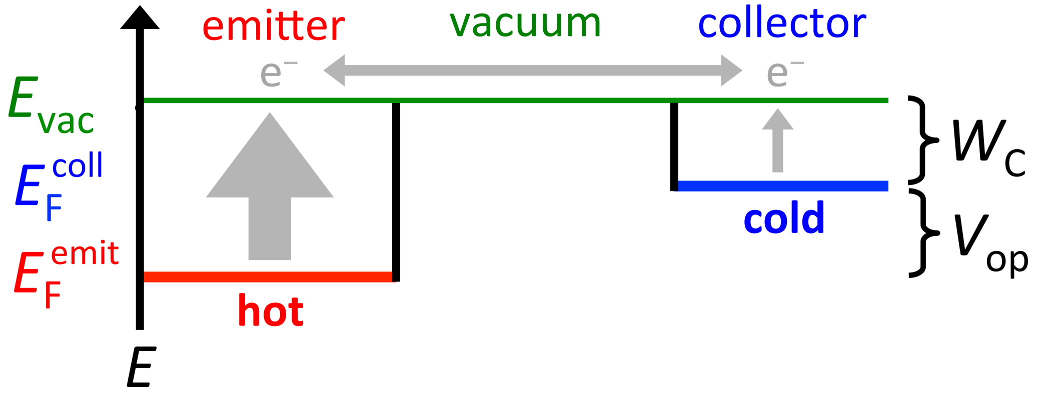
Global environment

	Li_i	LiN_4	$LiVN_6$
vacuum	0.00 eV (+5.59 eV)	−1.59 eV (+2.69 eV) *d*(Li-N) = 2.0 Å	−2.02 eV (+2.54 eV) *d*(Li-N) = 2.24 Å
diamond	6.32 eV (+0.22 eV)	0.91 eV (+0.27 eV) *d*(Li-N) = 1.72 Å	−0.94 eV (+0.28 eV) *d*(Li-N) = 2.01 Å

Bottom line: Is there an energetically favorable spot for Li^+ but not e^- in diamond?

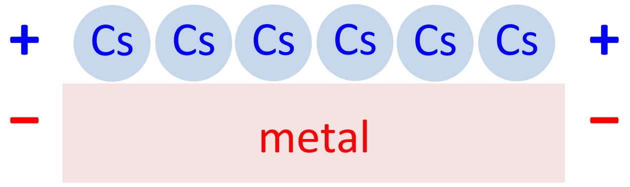
Motivation redux

Thermionic emission can generate electricity from heat,



[“Thermionic energy conversion”,
G. N. Hatsopoulos and
E. P. Gyftopoulos (1973)]

… but optimal room-temperature performance requires $W_C = 0.5$ eV.



vs.

H-terminated (111) surface (NEA)

n-type (P-doped) diamond

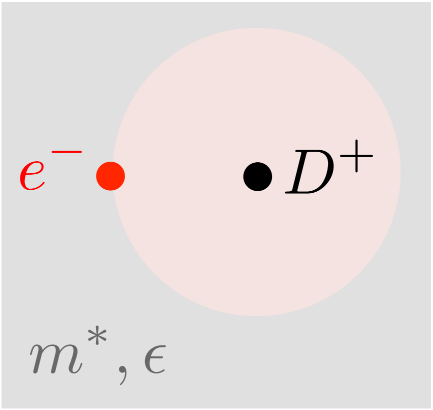
Cesium on metal surfaces
$W_C \geq 1.5$ eV

[Koeck *et al.*, Diam. Relat. Mater. **18**, 789 (2009)]
$W_C \approx 0.9$ eV

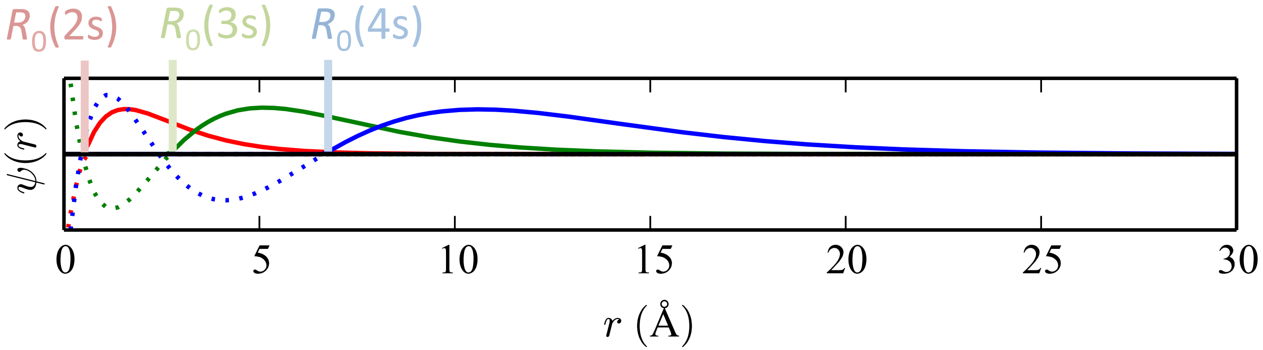
What fundamentally limits work functions / ionization potentials?

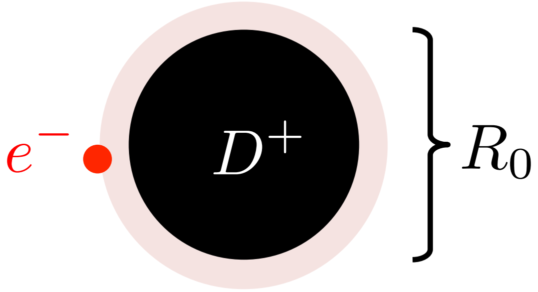
Ionization potential model

$$\left[-\frac{\nabla^2}{2}-\frac{1}{r}+V_{\mathrm{cc}}(r-R_0)\right]\psi(\mathbf{r})=-\Delta\psi(\mathbf{r})$$



Minimize Δ with a hard-wall potential at R_0,





$$m^* = \epsilon = 1$$

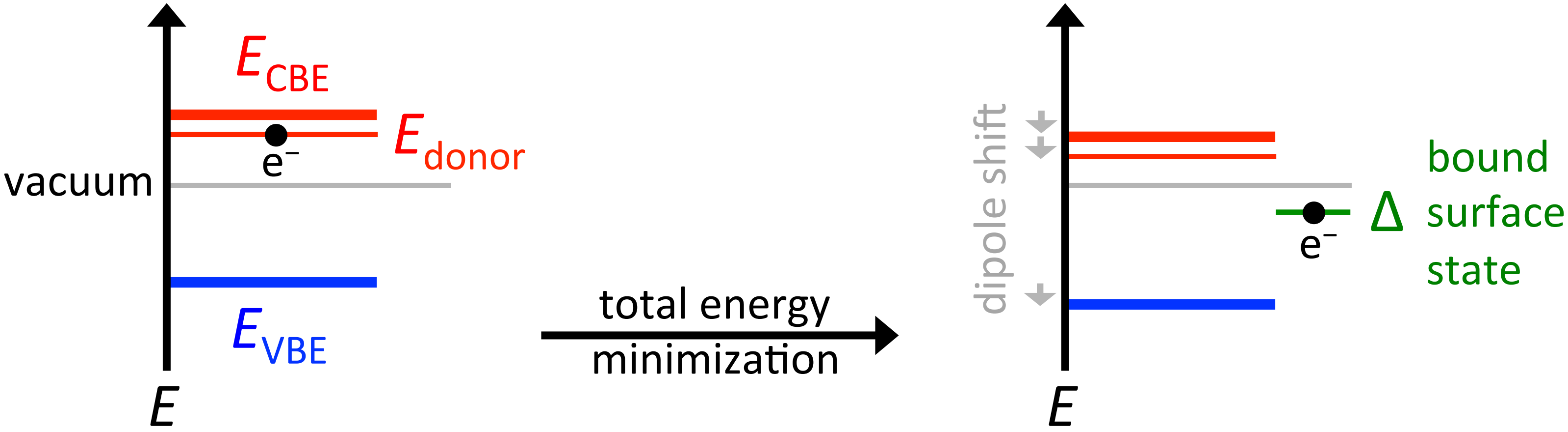
Simple trends in the large-R_0 solution,

$$\Delta \approx \frac{1}{R_0+7}$$

(R_0 = 25 Å for Δ = 0.5 eV)

Exact solution with hypergeometric functions?

Donor-in-diamond clusters



E_{CBE}

E_{donor}

e^-

vacuum

E_{VBE}

E

total energy minimization

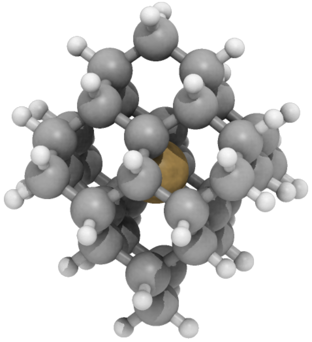
dipole shift

E

e^-

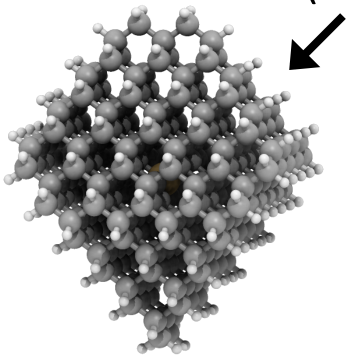
Δ bound surface state

(111) surfaces



smallest cluster simulated

$PC_{34}H_{36}$



largest cluster simulated

$PC_{264}H_{140}$

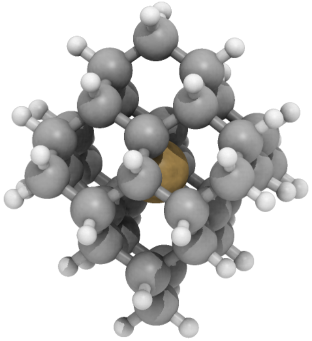
macroscopic cluster

(not simulated)

???

Methodology (ad hoc)

PBE-ε at interface between vacuum (ε = 1) & diamond (ε = 5.7)?

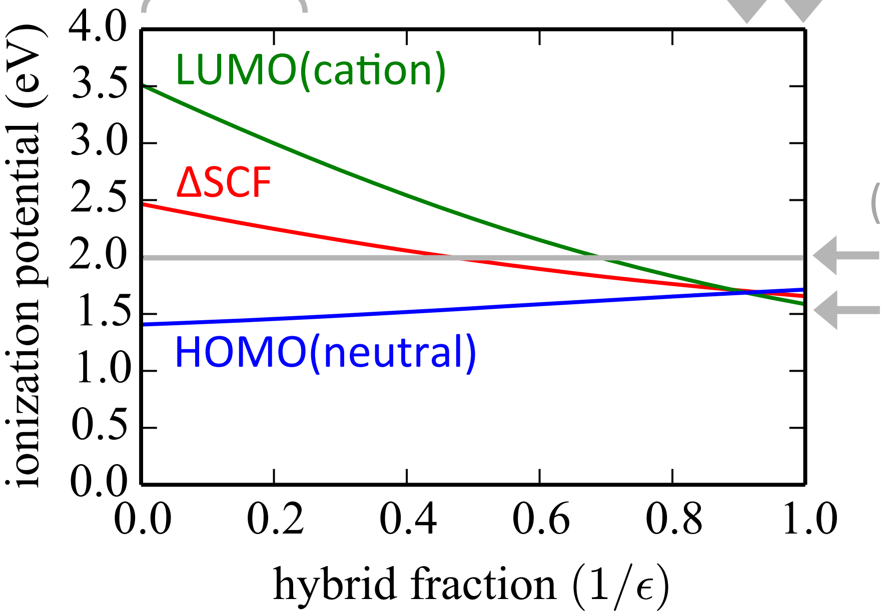


reference
cluster

good total energies
(PBE, PBE0, B3LYP, etc.)

Koopmans' compliance

correct asymptotic exchange
potential



(QMC value in progress)

MP2 value

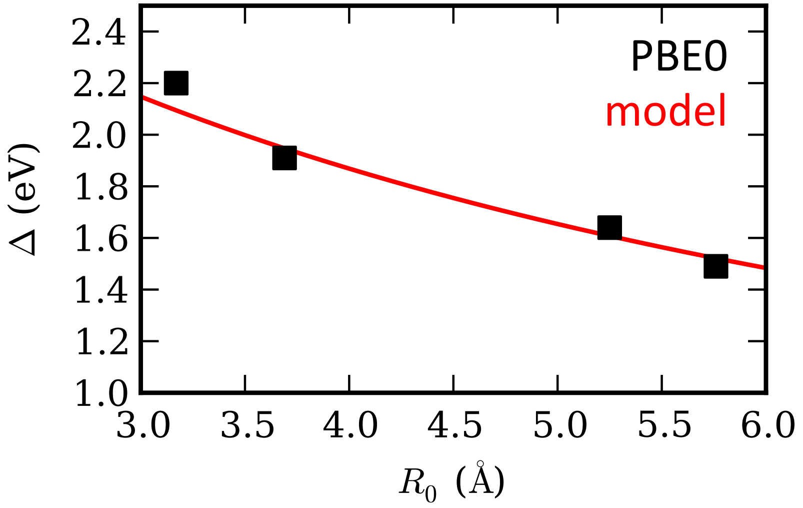
Hartree-Fock value

Electron correlation
contributes 25% to Δ,
25% variability in DFT

donor electron sees a different environment than electrons in diamond

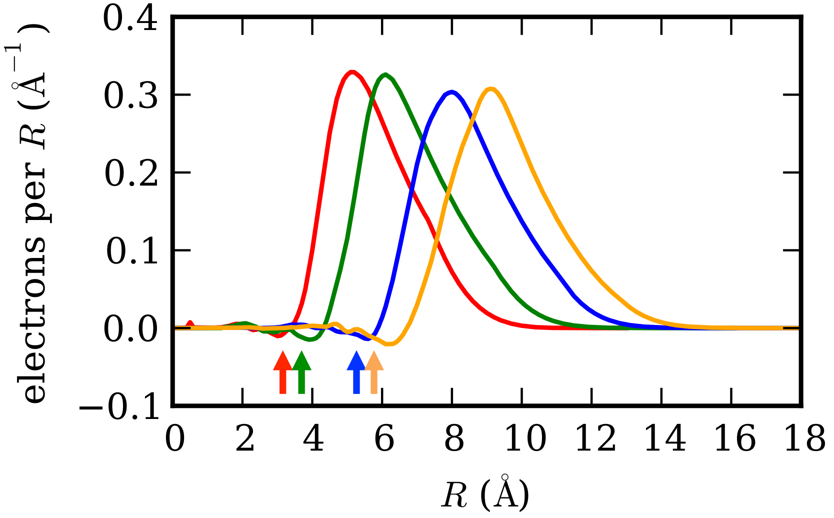
NWChem calculations: ΔSCF w/ PBE0 & cc-pVDZ basis (diffuse functions on H)

Numerical results



R_0 set by largest enclosed sphere within H-delineated surface plane

Surprising agreement between PBE0 and the spherical model!

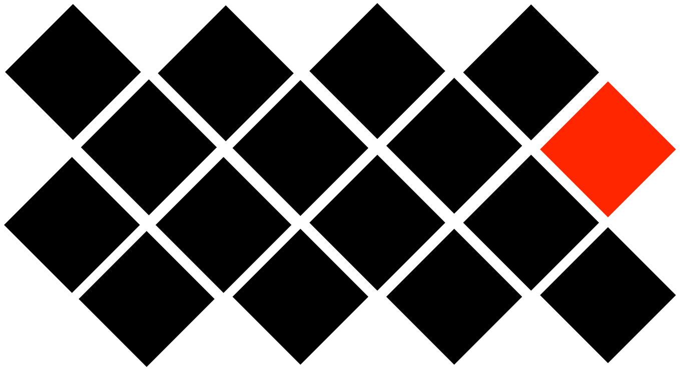


DFT reliably predicts autoionization of the donor electron to the surface

Further agreement between DFT and the model! (a simple system)

From clusters to surfaces

Simple trade-off between *W* & surface electron density,



(Hypothetically) tile surface with clusters

surface electron density $\propto R_0^{-2}$

work function $\propto R_0^{-1}$

W^2 / surface electron density $\propto$ constant

Practical limit is the metal-insulator transition in diamond,

Well-studied transition for *p*-type, B-doped diamond rescaled for *n*-type:

[T. Klein *et al.*, Phys. Rev. B **75**, 165313 (2007)]

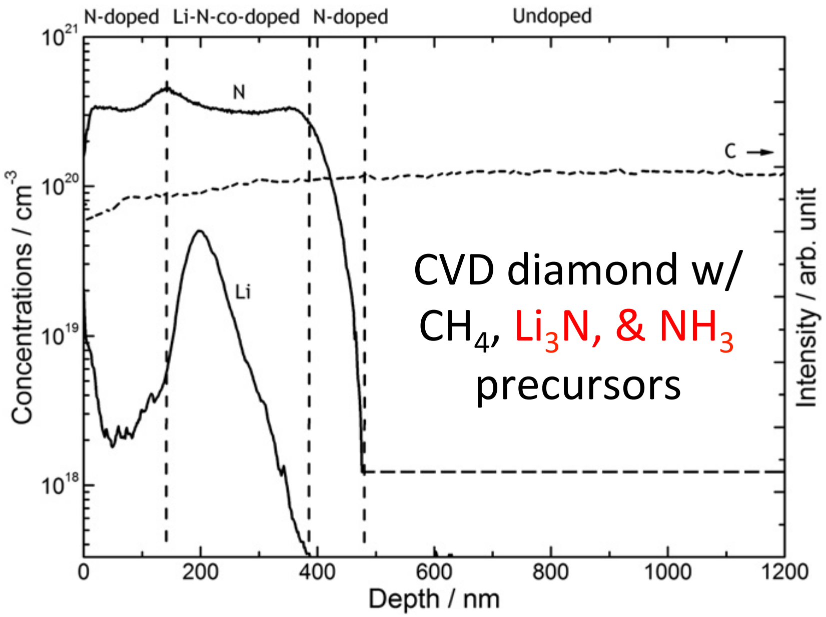
$$\rho_{\text{donor}} \geq 5\times10^{19}\ \text{cm}^{-3} \rightarrow R_0 \leq 17\ \text{Å} \rightarrow W \geq 0.7\ \text{eV}$$

crude estimate

Other semiconductors with negative electron affinity? SiC?

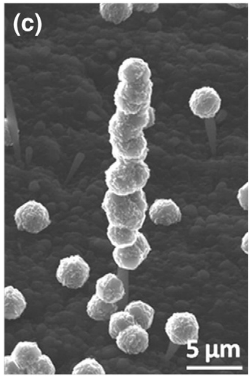
Outlook

Experimental



CVD diamond w/ CH_4, Li_3N, & NH_3 precursors

[Othman *et al.*, Diam. Relat. Mater. **44**, 1 (2014)]



N-doped diamond microcrystals w/ *W* = 2.2 eV

[Sherehiy *et al.*, Diam. Relat. Mater. **50**, 66 (2014)]

Theoretical

To understand HPHT synthesis,

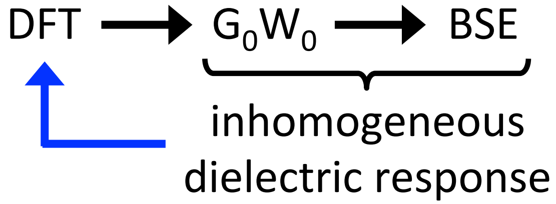
Li-N defect chemistry in diamond

To understand CVD synthesis,

large precursors in CVD growth conditions

To better trust theoretical predictions …

What happens when DFT doesn't put electrons in the right ***place***?



$$\text{DFT} \longrightarrow \underbrace{G_0W_0 \longrightarrow \text{BSE}}_{\text{inhomogeneous dielectric response}}$$

Self-consistent RPA of ground & excited states as a ***minimal*** trustworthy model?