Efficient algorithms for the electronic structure of nanocrystals

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Outline:

I. A filtering approach to solve the self-consistent Kohn-Sham equation

II. Application to P-doped Si nanocrystals

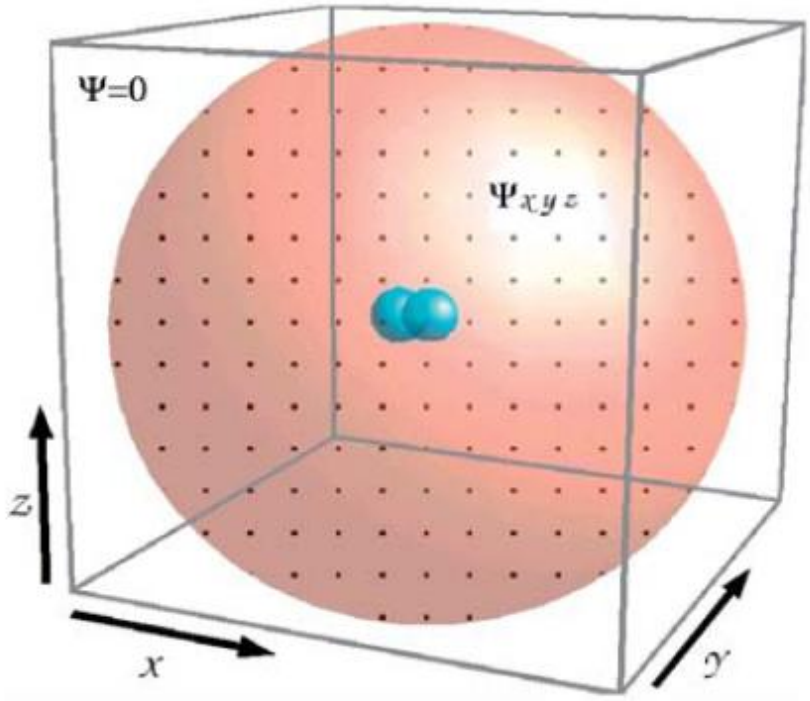
The Kohn-Sham equation can be solved on a real space grid:

$$\left(-\frac{\nabla^2}{2}+V_{\mathrm{ps}}(\boldsymbol{r})+V_{\mathrm{H}}(\boldsymbol{r})+V_{\mathrm{xc}}[\rho(\boldsymbol{r})]\right)\varphi_i(\boldsymbol{r})=\varepsilon_i\varphi_i(\boldsymbol{r}) \quad , \ \varphi_i(R)=0$$

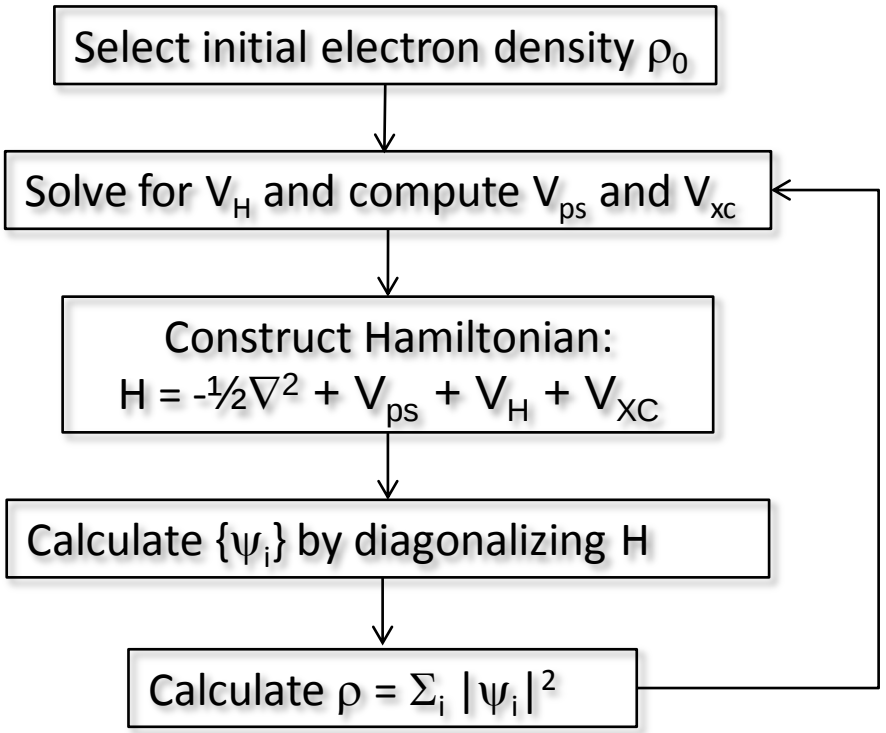
The Laplacian operator ∇^2 can be evaluated using a high order finite differencing method:

$$\nabla^2\varphi(x,y,z)=\frac{1}{h^2}\sum_{k=-M}^{M}\sum_{l=-M}^{M}\sum_{m=-M}^{M}[C_k\varphi(x+kh,y,z)$$

$$+C_l\varphi(x,y+lh,z)+C_m\varphi(x,y,z+mh)]$$



A flow chart of solving the self-consistent Kohn-Sham equation



Filtering approach to solve the Kohn-Sham problem

•Only the electron density ρ is needed as an input to the next self-consistent iteration, the knowledge of each intermediate eigenstates φ_i is not required.

•If $\{\varphi_i\}$ are rotated by a unitary operator U, $\varphi'_i = U_{ij}\,\varphi_j$ then

$$\rho(\boldsymbol{r}) = \sum_{i=1}^{\text{occup}} |\varphi'_i(\boldsymbol{r})|^2 = \sum_{i=1}^{\text{occup}} |\varphi_i(\boldsymbol{r})|^2$$

•It is sufficient to find the subspace spanned by the occupied states to calculate ρ

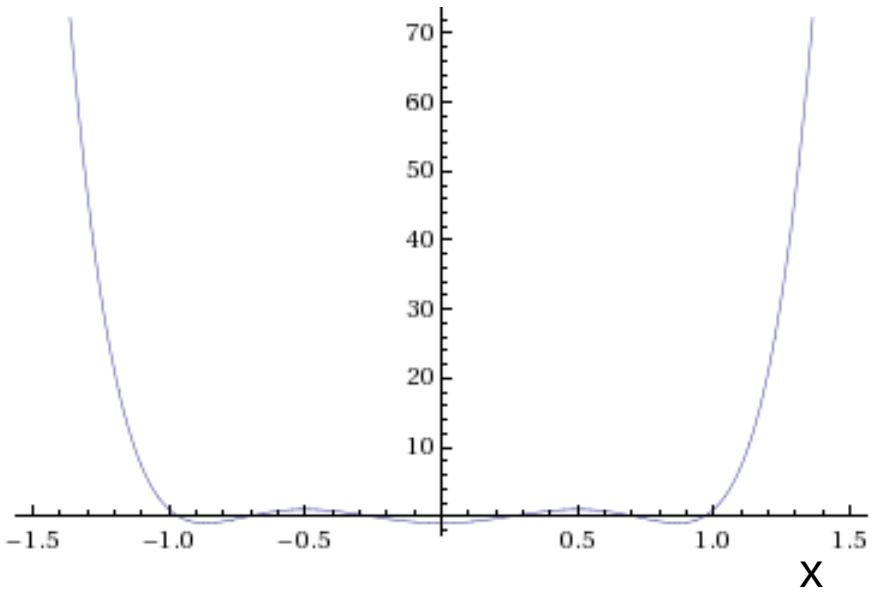
•Instead of diagonalizing the Hamiltonian for each iteration, it is sufficient to simply optimize the occupied eigen subspace.

Chebyshev polynomial filtered subspace iteration

•Want a polynomial filter P(*H*) for the set of eigenstates $\{\psi_i\}$, such that the span of $\{\psi_i\}$ can progressively approach the occupied eigen subspace of *H*

•A choice for the polynomial P is the Chebyshev polynomial T_n

Chebyshev polynomial $T_6(x)$



Chebyshev polynomials T_n are very fast growing outside [-1,1]

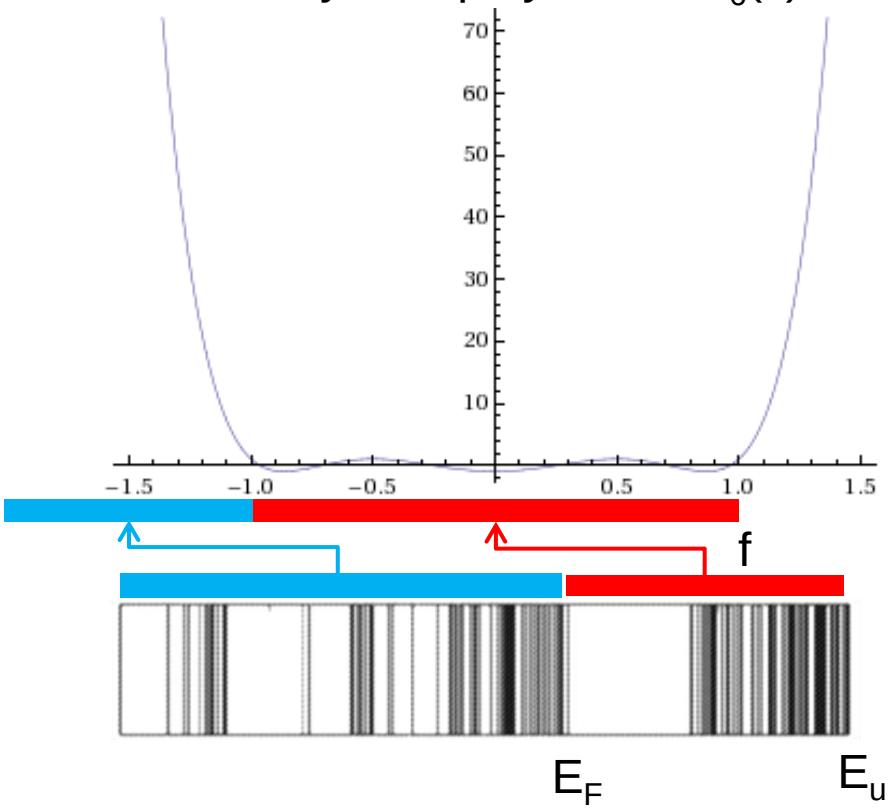
$T_n(H)\{\psi_i\}$ will therefore suppress the eigenstates with E_i between [-1,1]

Recurrence relation:

$$T_0(x) = 1$$
$$T_1(x) = x$$
$$T_{n+1}(x) = 2xT_n(x) - T_{n-1}(x)$$

Y. Zhou, Y. Saad, M. L. Tiago, J. R. Chelikowsky, J. Comp. Phys., 219 (2006) pp. 172-184
Y. Zhou, Y. Saad, M. L. Tiago and J. R. Chelikowsky. Physical Review E, 74 066704-1-8, (2006)

Chebyshev polynomial $T_6(x)$



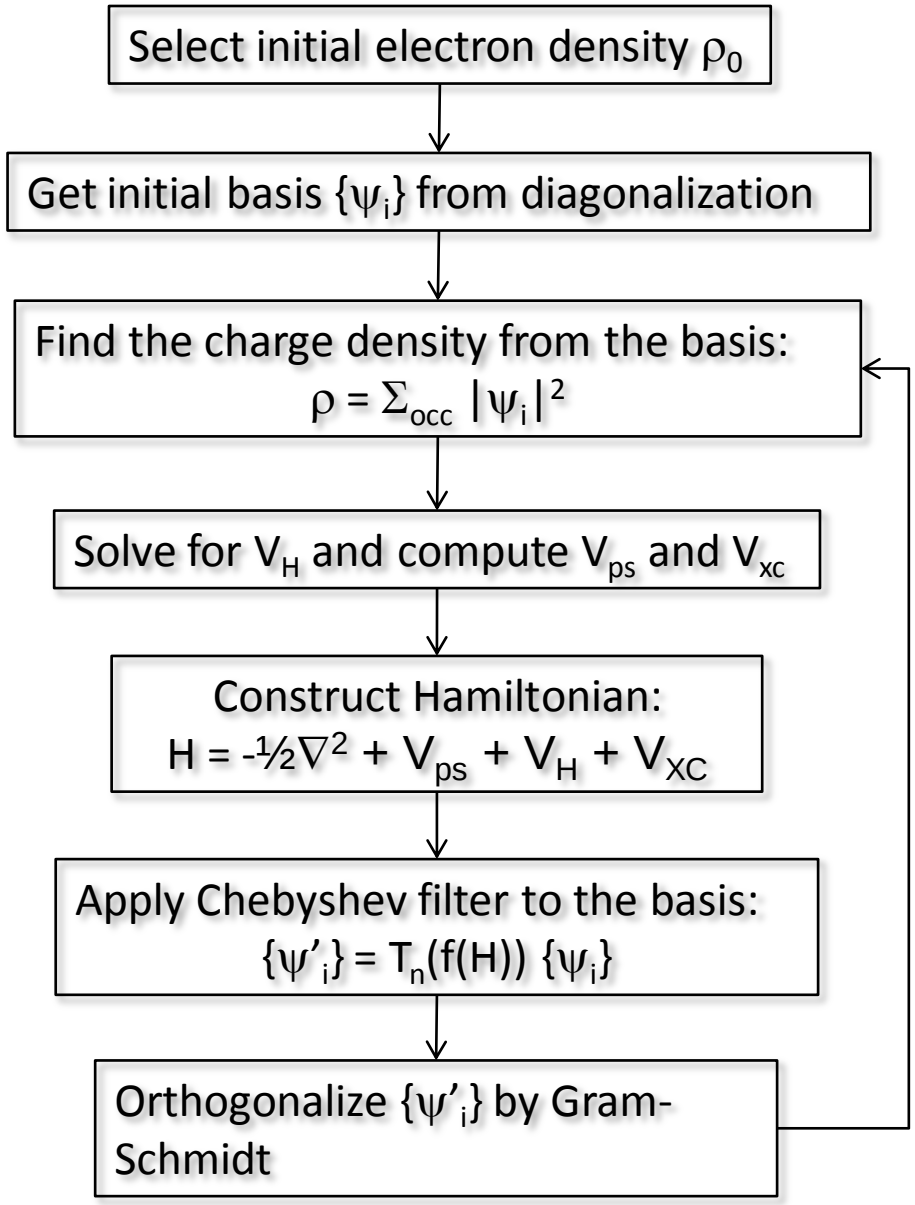
Eigenvalue spectrum

We can define an affine mapping f:

$$f(E) = \frac{E - (E_u + E_F)/2}{(E_u - E_F)/2}$$

such that the energy interval $[E_F, E_u]$ is mapped to [-1,-1]

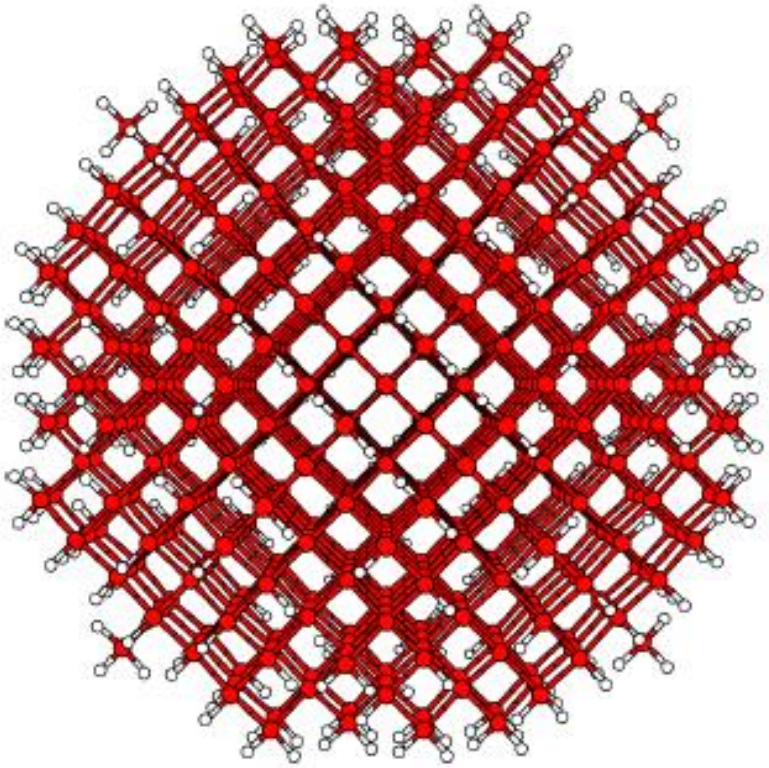
The filter $T_n(f(H))$ operating on $\{\psi_i\}$ will suppress all the eigenstates with energy between $[E_F, E_u]$



The algorithm is implemented in PARSEC(Pseudopotential Algorithm for Real-Space Electronic Calculations)

Website:
http://parsec.ices.utexas.edu

An atomic model of a $Si_{525}H_{276}$ nanocrystal



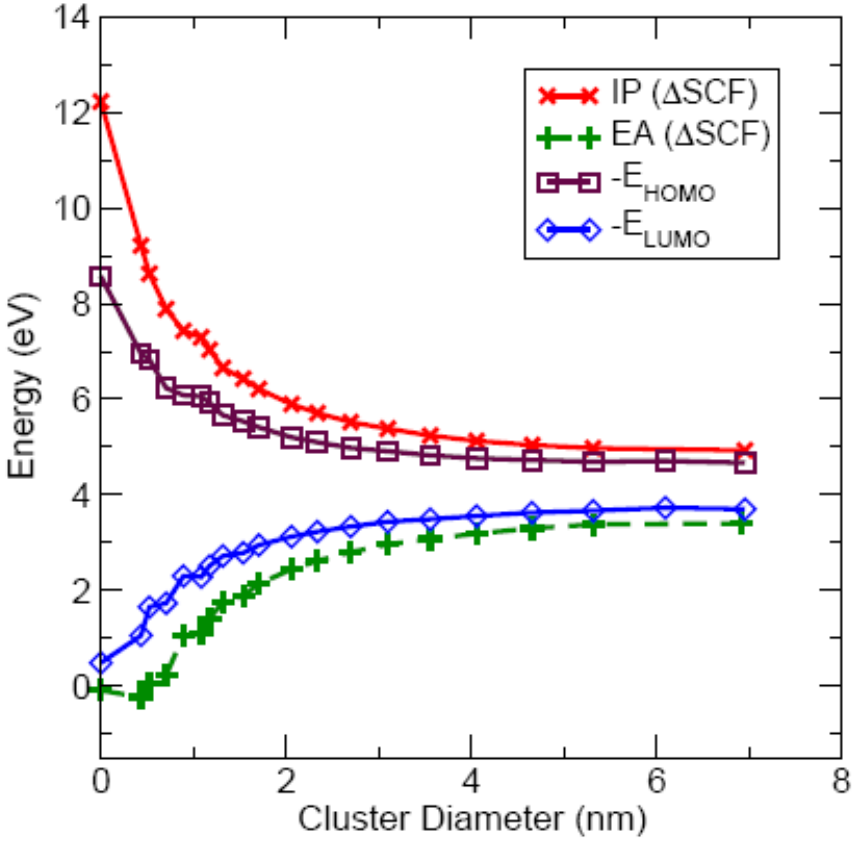
$Si_{525}H_{276}$
Hamiltonian size 292,584 x 292,584
Number of eigenstates: 1,194
16 processors

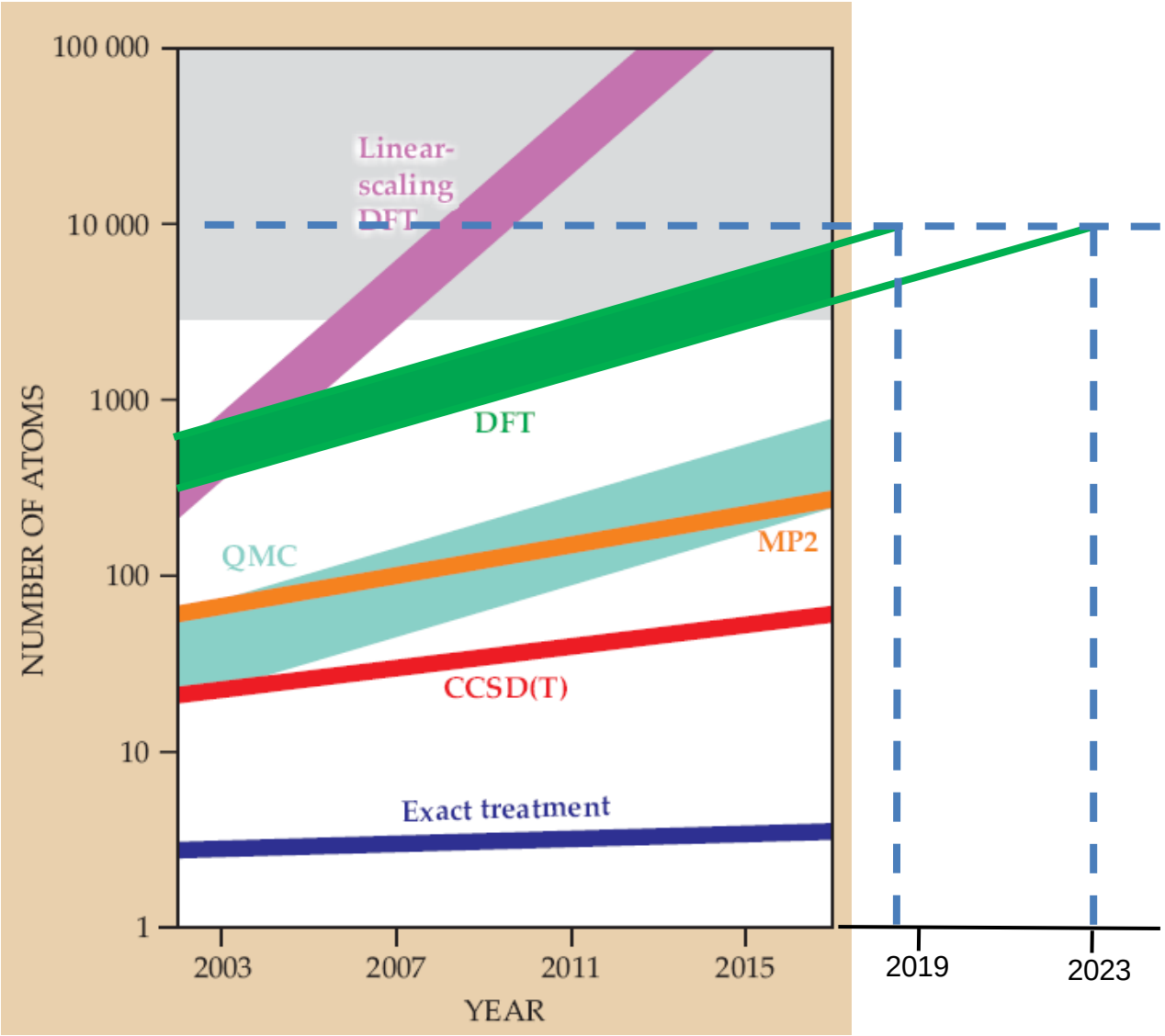
Method	SCF Its	CPU(s)
Filtering	11	543
TRLan	10	2755
DIAGLA	10	8751

We studied H-passivated Si nanocrystals up to a diameter of 7 nm($Si_{9041}H_{1860}$)

•The evolution of the electronic structure can be studied from small nanocrystals all to way to sizes that are nearly bulk-like

•Our algorithm can be applied to various types of systems: SiGe nanocrystals, GaAs nanocrystals, Fe clusters, Zn-doped InP nanowires

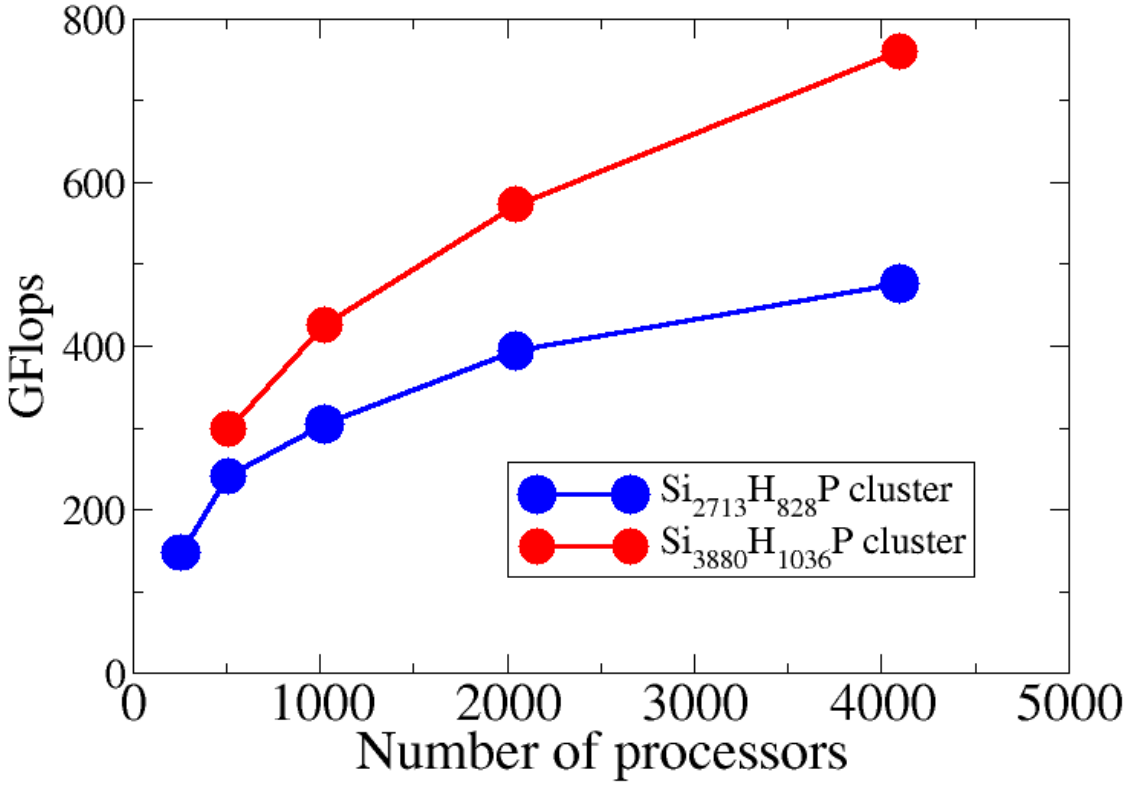




Martin Head-Gordon, and Emilio Artacho
Physics Today -- April 2008 Volume 61, Issue 4, pp. 58-63

NERSC Cray XT4 Franklin

19,320 computing cores
Opteron 2.6 GHz processors

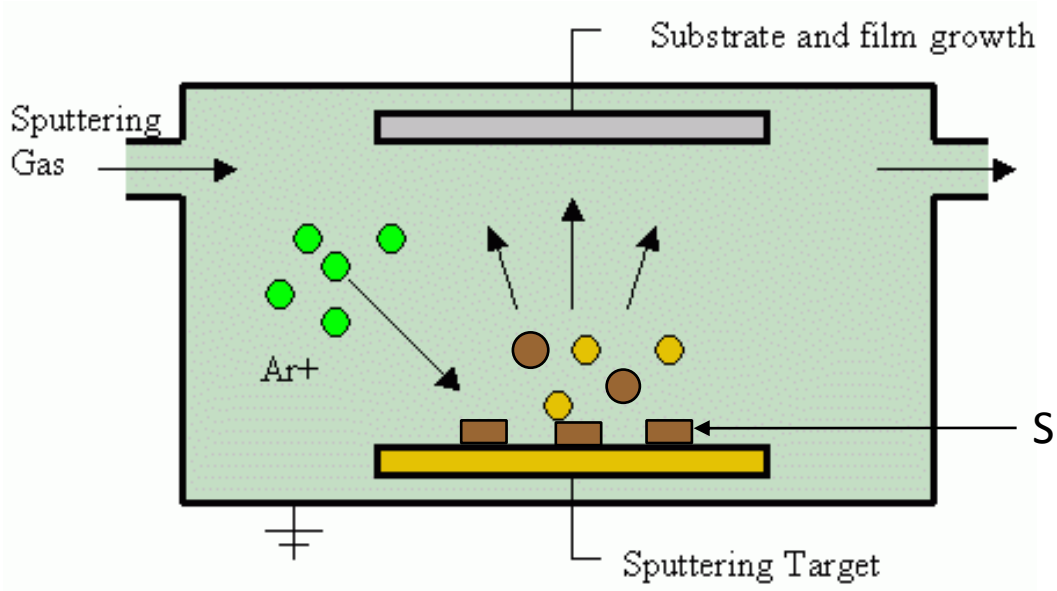


Application: P-doped Si nanocrystals

- Experimental synthesis of P-doped Si nanocrystals
- Theoretical study of the defect state
  - Shape of defect wave function
  - binding energy
- Energetics of P position inside Si nanocrystals
- An effective mass theory for P-doped nanocrystals

(T.-L. Chan, M. L. Tiago, E. Kaxiras, J. R. Chelikowsky, Nano Lett.8(2), 596-600, 2008)

Synthesis of P-doped Si nanocrystals



Sputtering target: PSG(phosphosilicate glass, P-doped silica (SiO_2))

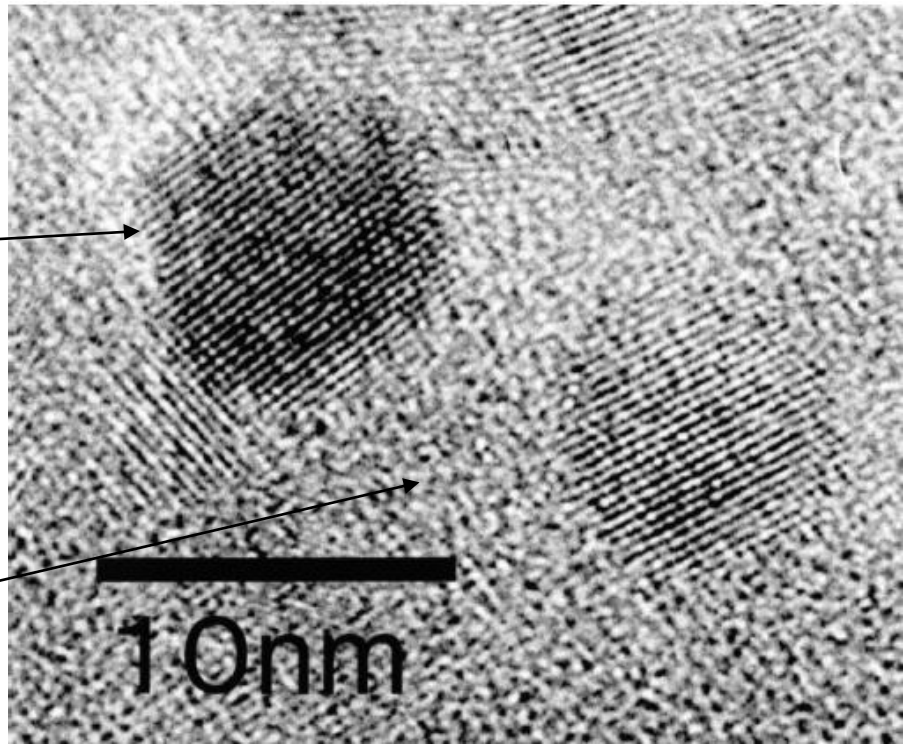
Substrate: quartz

- Si chips and PSG are co-sputtered in Ar gas
- The deposited film is then annealed in N_2 gas at 1200^oC
- Si nano-clusters will grow during annealing

TEM image of doped Si nanocrystals in BPSG thin film

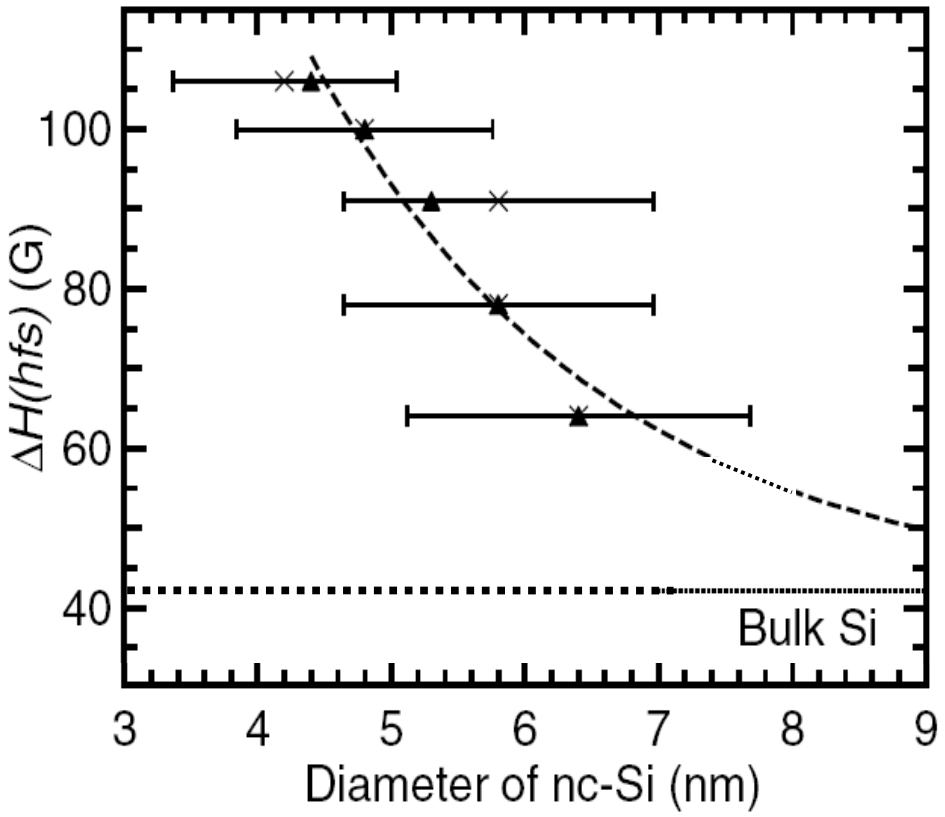
Si nanocrystals have
- lattice fringes correspond to {111} planes of Si
- roughly spherical in shape

BPSG thin film



M. Fujii, K. Toshikiyi, Y. Takase, Y. Yamaguchi, S. Hayashi, J. Appl. Phys. 94, 1990 (2003)

Experimental measurement of hyperfine splitting



M. Fujii, A. Mimura, S. Hayashi
Phys. Rev. Lett. 89, 206805(2002)

- Hyperfine splitting is due to the interaction between the nucleus spin and the electron spin

- For a P-doped Si nanocrystal, only P contributes to hyperfine splitting, since Si does not have nucleus spin.

- Isotropic hyperfine constant

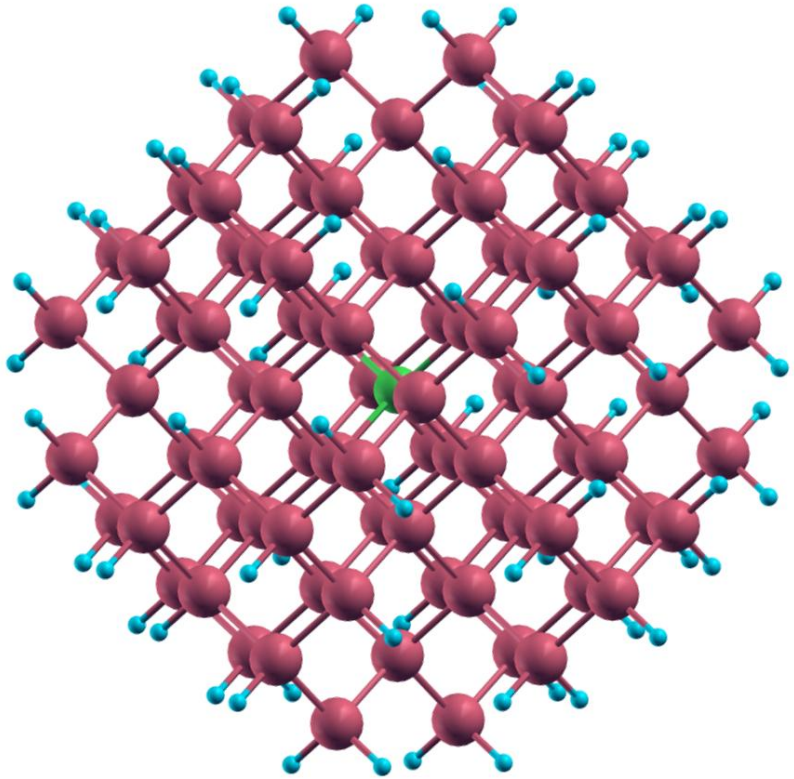
$$a = 2/3\ \mu_0 g_e \mu^e g_i \mu^i |\psi(\mathbf{R})|^2$$

measures how localized the defect wave function is on the P atom

Calculation Setup:

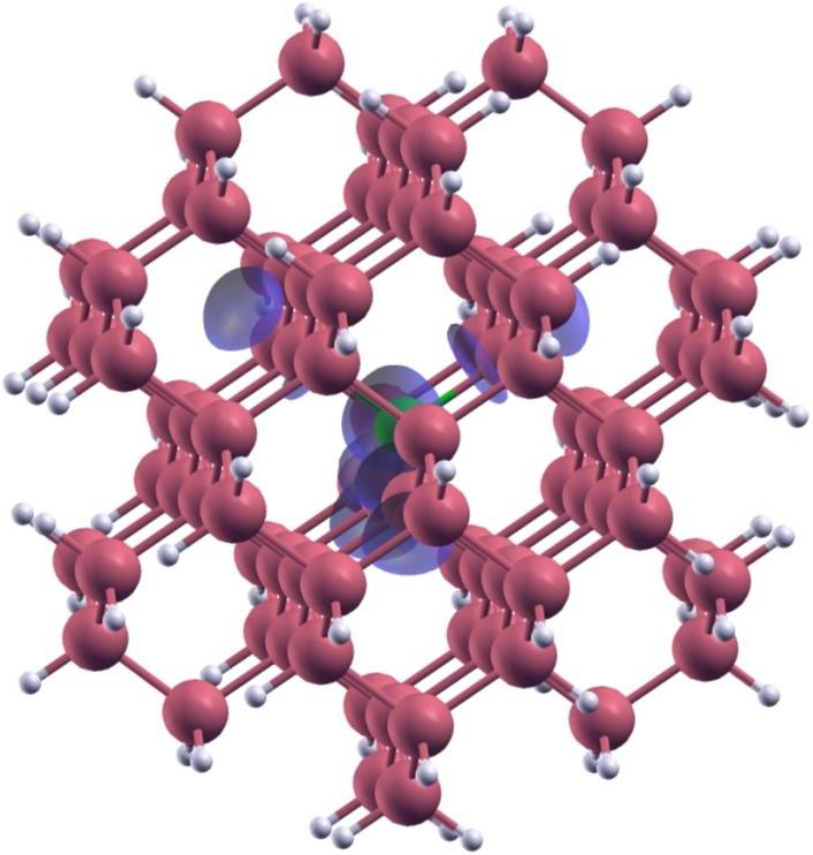
- Grid spacing is chosen to be 0.55 a.u.
- Norm-conserving Troullier-Martins pseudopotentials are used
- There is 10 a.u. of vacuum space around the Si nanocrystal.

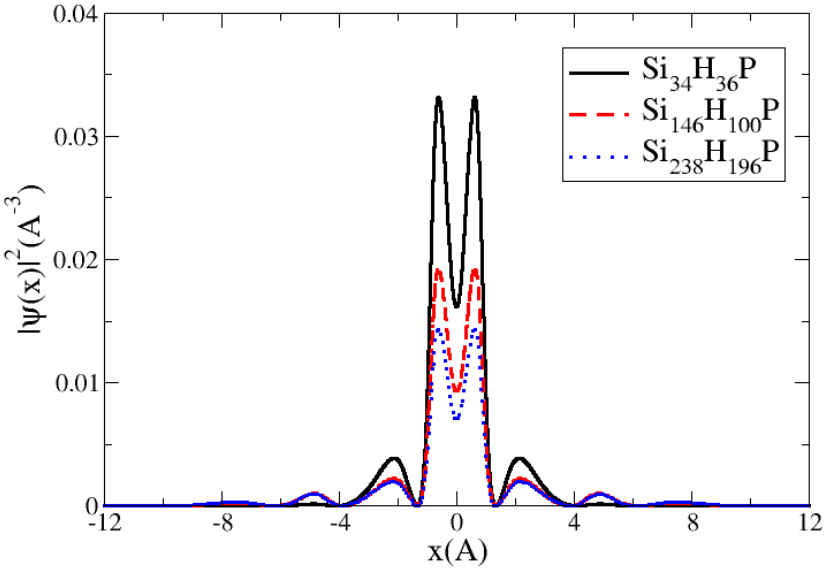
An atomic model of a $Si_{86}H_{76}P$ nanocrystal

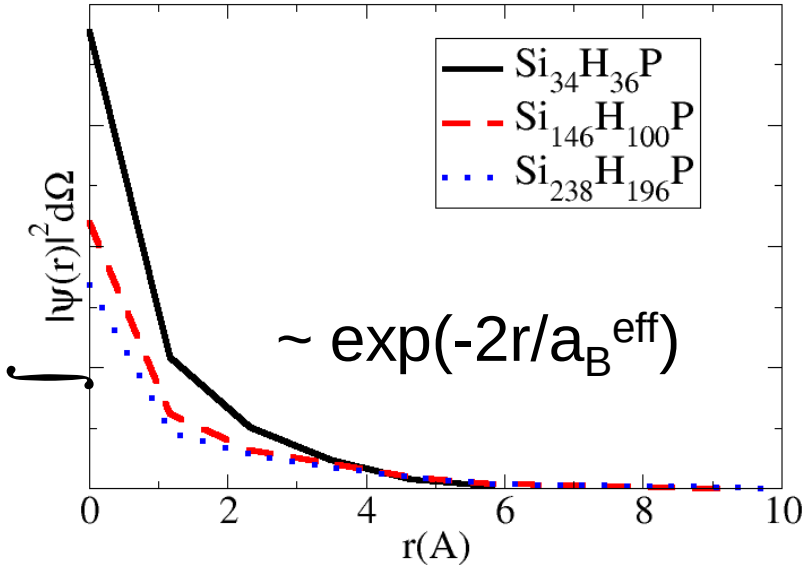


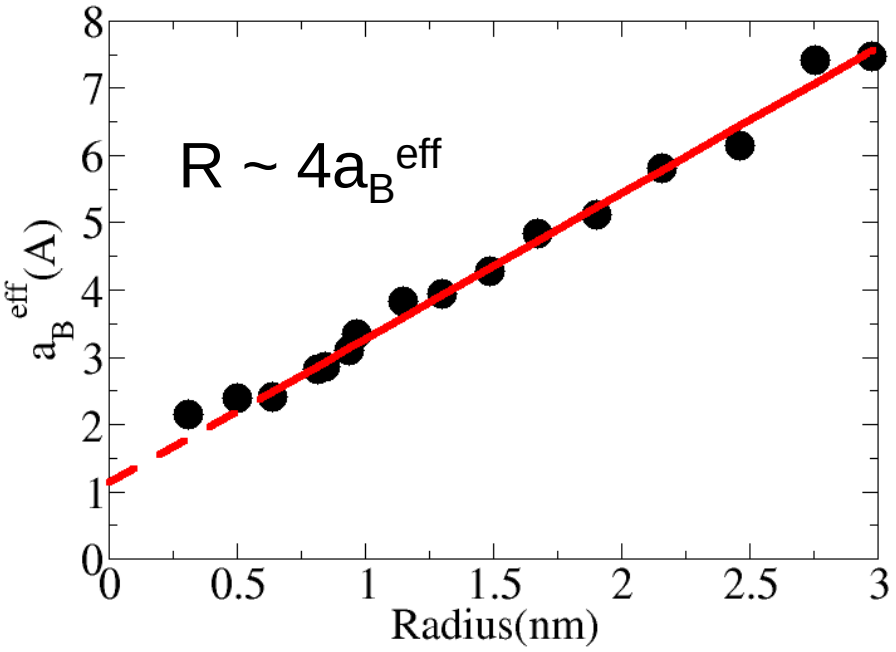
Theoretical study of the defect wave function in a P-doped Si nanocrystal

Plot of the defect charge density

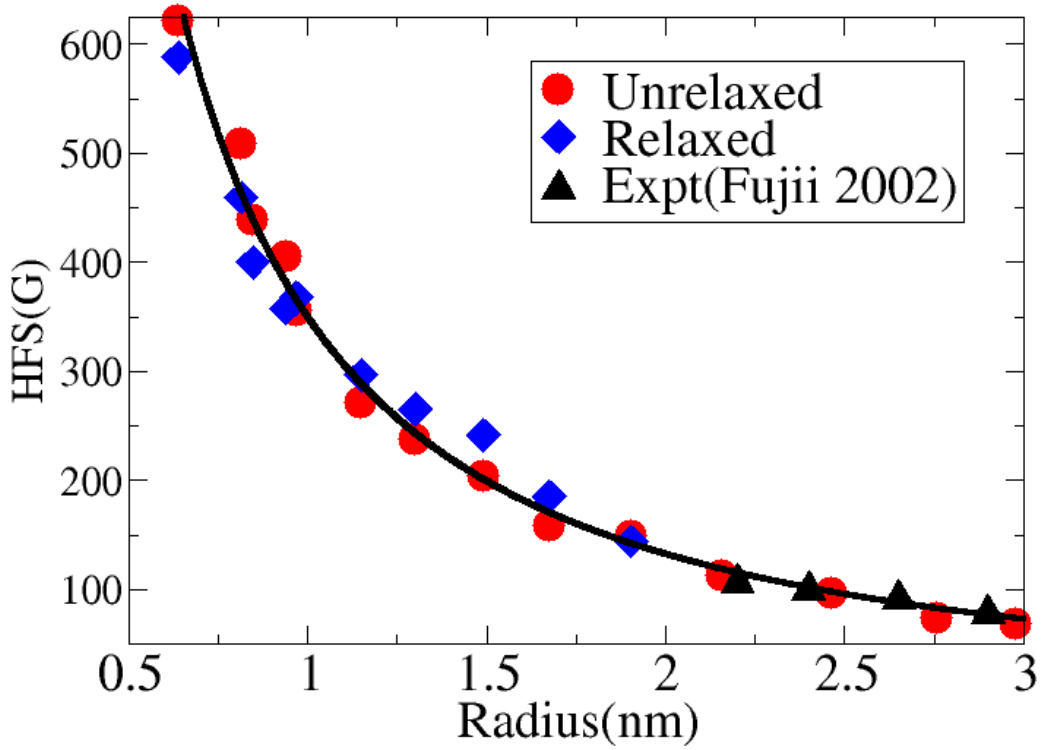








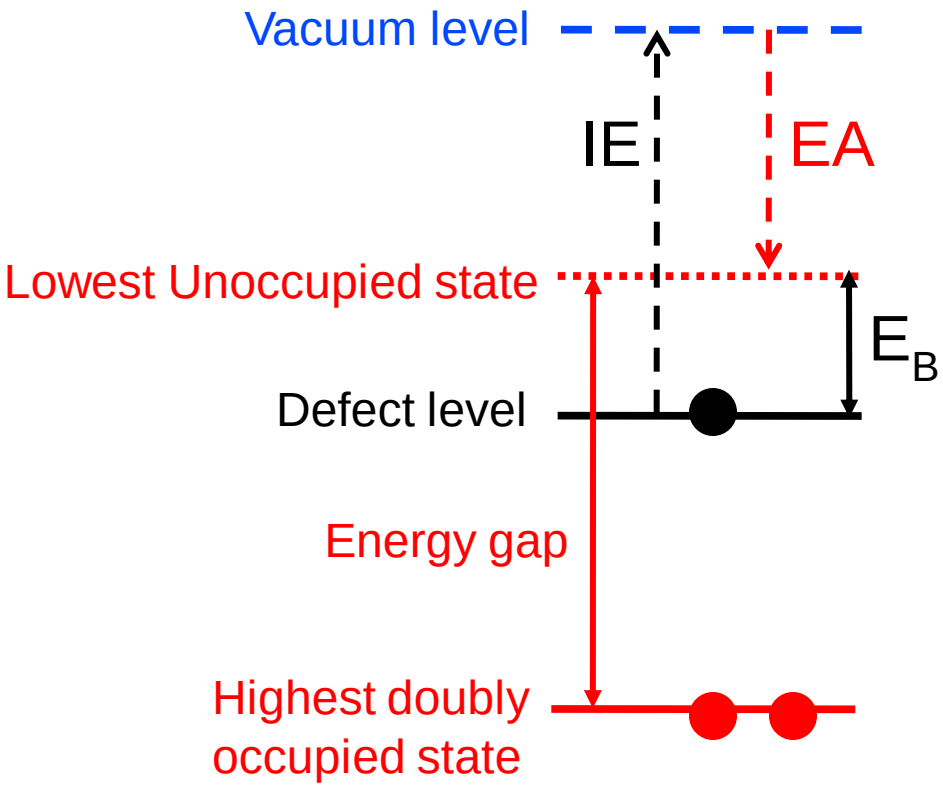
- a_B^{eff} scales linearly with R(roughly, R ~ $4a_B^{eff}$)
- When R~10nm, $a_B^{eff} \rightarrow a_B^{bulk}$(~$a_B^0\ \varepsilon/m^* = 2.3$ nm)
- P-doped Si nanocrystals need to be at least ~ 10 nm in order to be bulk-like

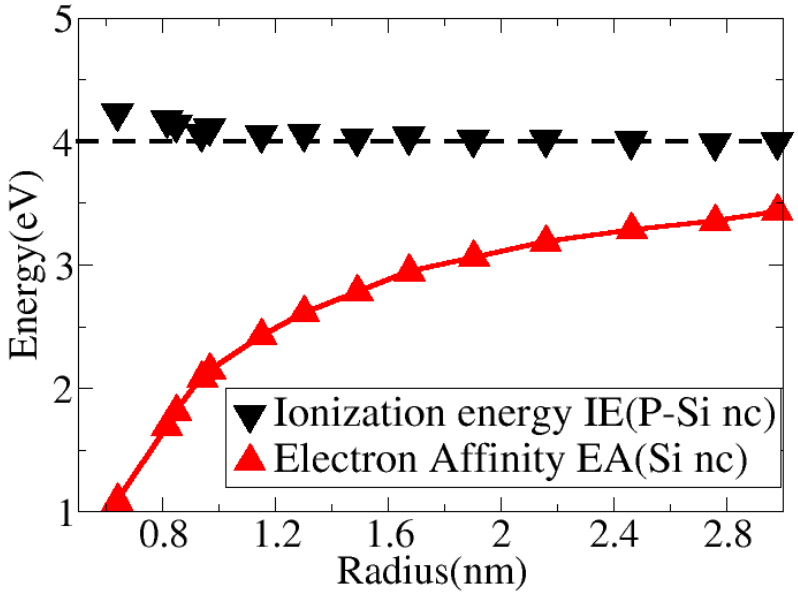


•Effect of quantum confinement: The defect wave function becomes more localized on the P atom as size decreases, resulting in higher HFS

•Efficient algorithms enable us to calculate large enough nanocrystals to compare with experimental data. And there is very good agreement between our calculations and the experiment.

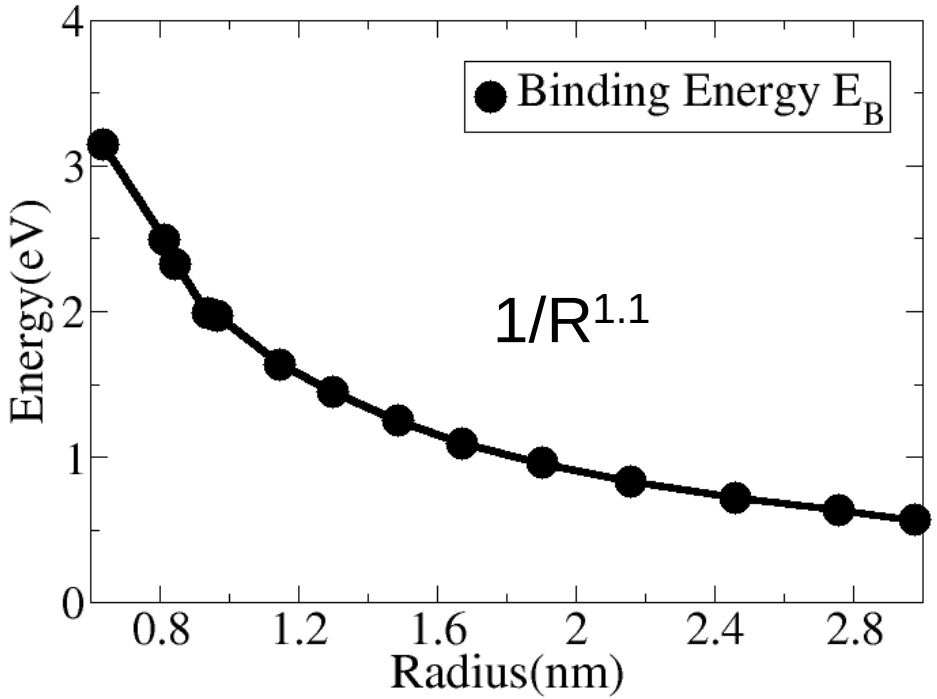
Study of the binding energy of the dopant electron





The binding energy of the dopant electron by P in a Si nanocrystal

E_B = (Ionization Energy of P-Si nanocrystal) – (Electron affinity of pure Si nanocrystal)

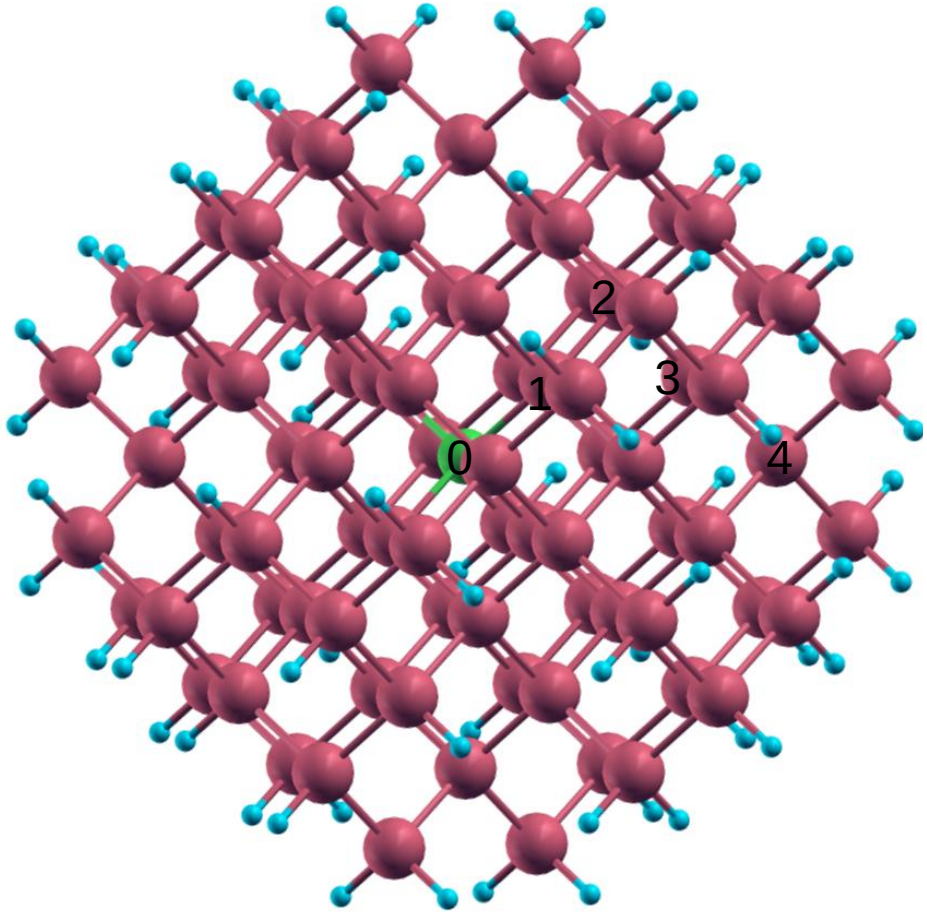


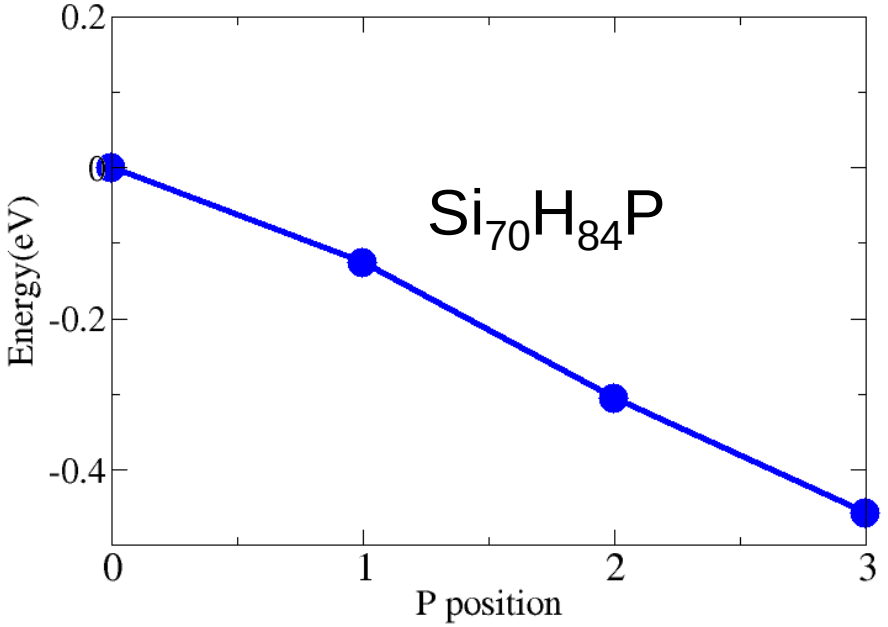
•The dopant electron strongly binds to the P atom as nanocrystal size decreases

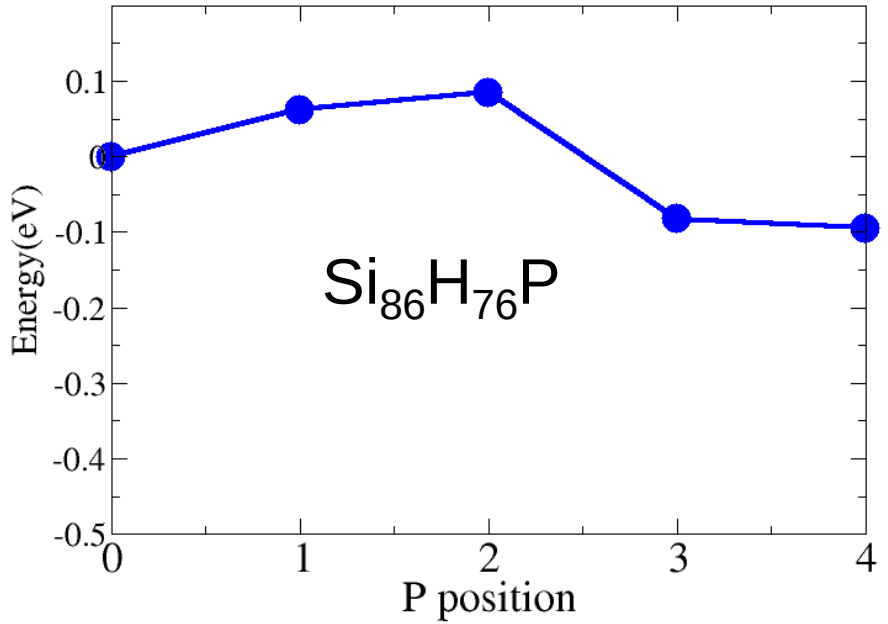
•For P to be a shallow donor($E_B \leq$ a few kT at room temperature), the diameter of the Si nanocrystal needs to be larger than 20 nm

Location of P in Si nanocrystal

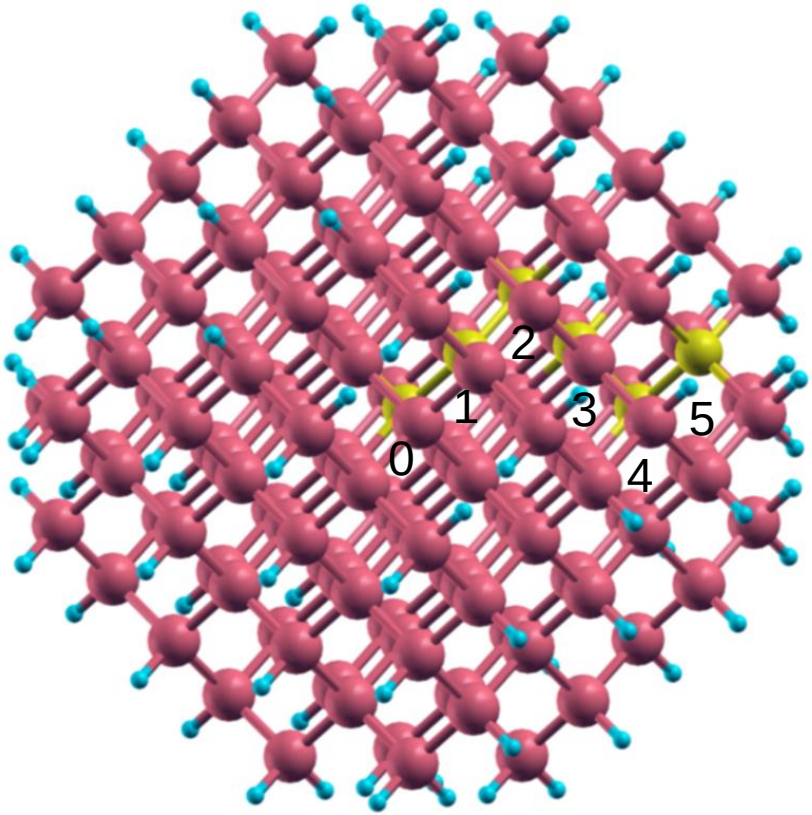
A schematic figure illustrating the different positions for doping a P atom into a Si nanocrystal

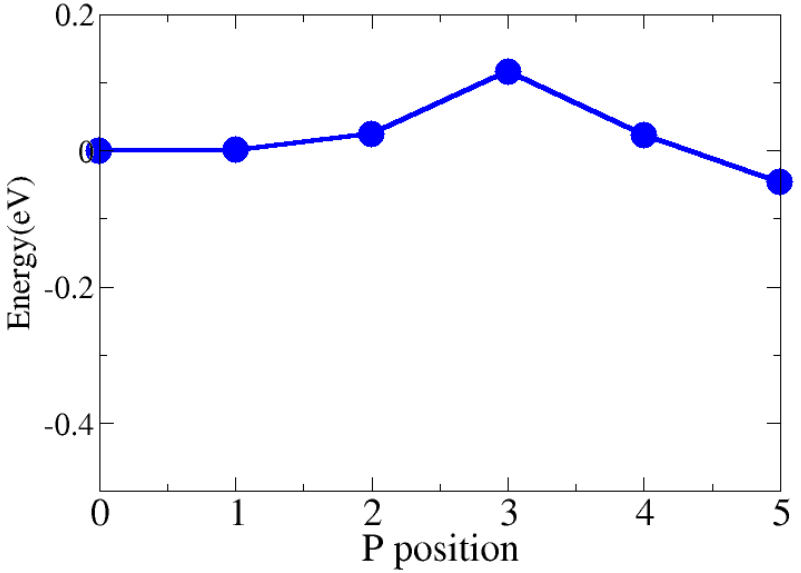


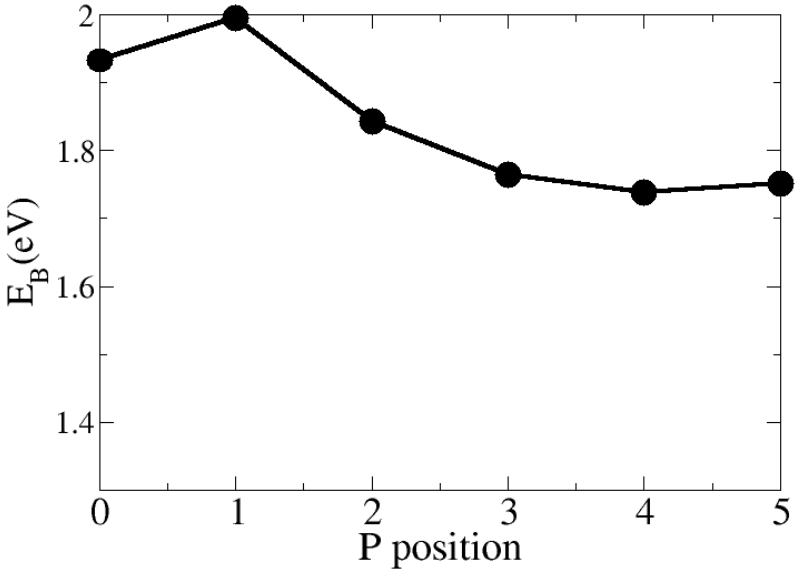




$Si_{238}H_{196}P$







For larger Si nanocrystal(~2 nm diameter), both the center and the surface of the Si are stable positions for P

Effective mass theory for doped-semiconductor nanocrystals

$$V(r) = \begin{cases} \dfrac{-1}{\epsilon(R)r} + V_0 & \text{for } r \le R; \\ \dfrac{-1}{r} & \text{otherwise} \end{cases}$$

The size-dependence of the dielectric constant ε is taken from Penn's model:

$$\epsilon(R) = 1 + \frac{\epsilon_b - 1}{1 + (\alpha/R)^n}$$

The Hamiltonian $H = -1/(2m^*)\,\nabla^2 + V(r)$

We can minimize the energy of H with the trial function:

$$\psi = \sqrt{\pi/a_B^3}\,\exp(-r/a_B)$$

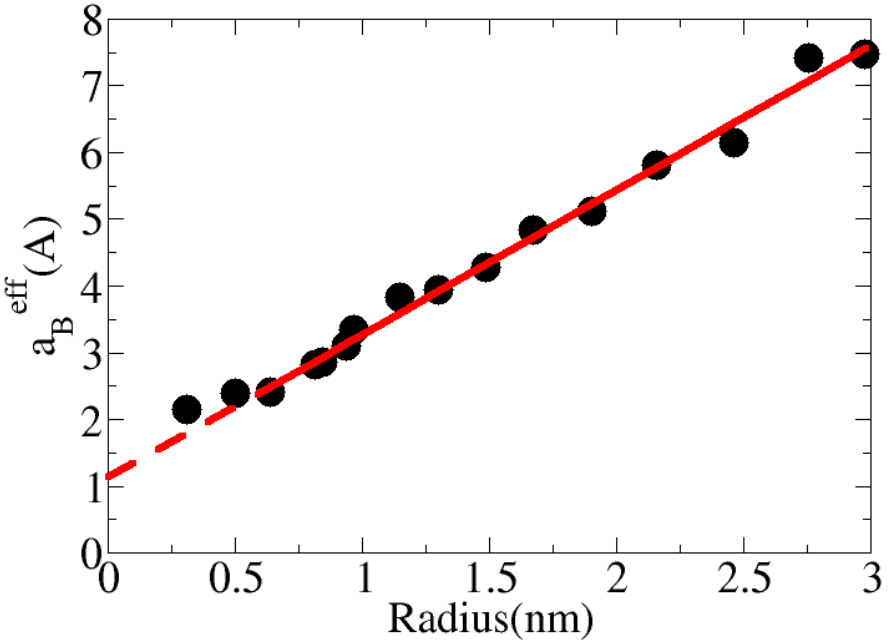
and treat a_B as a variational parameter.

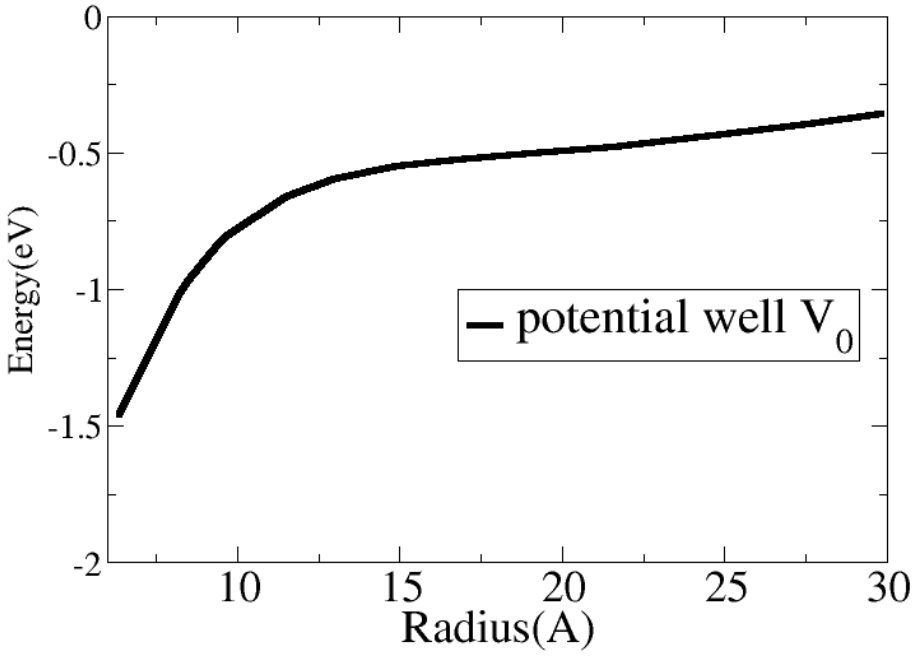
By minimizing $E = \langle\psi|H|\psi\rangle$,

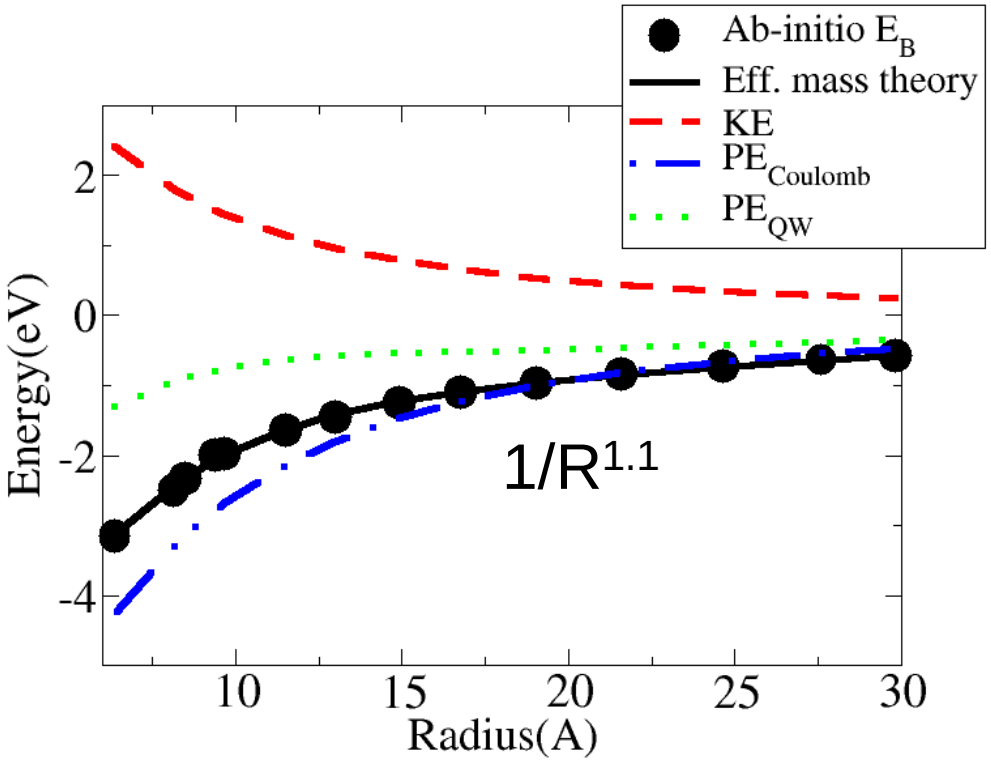
$$V_0 = -a_B\, e^{(2R/a_B)}\, (\varepsilon/m^* - a_B)/(4\varepsilon R^3)$$

The parameters α and n in $\epsilon(R) = 1 + \dfrac{\epsilon_b - 1}{1 + (\alpha/R)^n}$

are obtained by fitting E to our calculated binding energy E_B from first-principles. (fitted α = 54Å and n = 1.6 for the Penn's model)







•The binding energy calculated using effective mass theory can be fitted very well to our first-principles results

•E_B scales like the Coulomb interaction 1/R for a wide range of nanocrystal sizes

•For small nanocrystals, the $1/R^2$ dependence due to the kinetic energy of quantum confinement gets more prominent

Conclusions:

- The self-consistent Kohn-Sham equation can be solved efficiently in real space with damped Chebyshev-polynomial filter subspace iteration

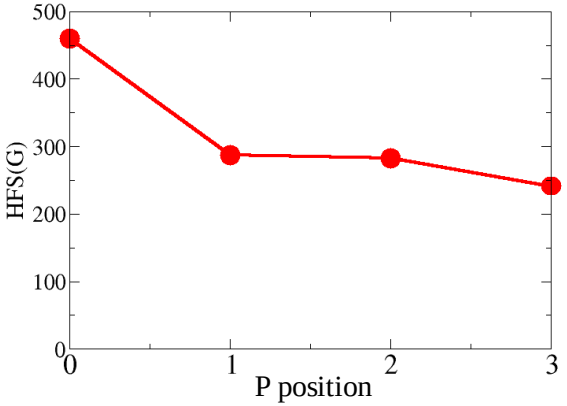
- Up to 10,000 atoms can be calculated from first-principles. We studied P-doped Si nanocrystals up to 6 nm in diameter, and our calculated results have very good agreement with experimental data.

Our research is supported by:

Computational resources are provided by:

Dependence of HFS on P position

$Si_{70}H_{84}P$



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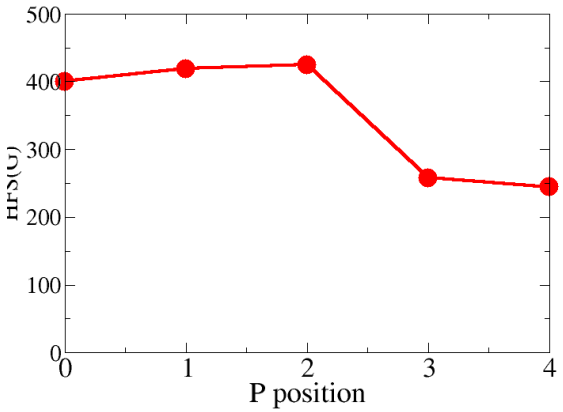

$Si_{238}H_{196}P$