

# **Scalable Computational Tools for Discovery and Design -- Excited State Phenomena in Energy Materials**

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# Principal Investigators: Computational Scientists



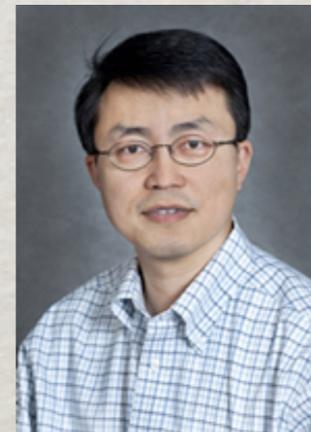
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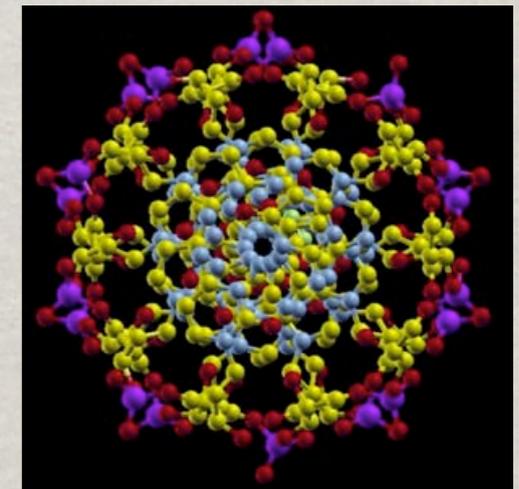
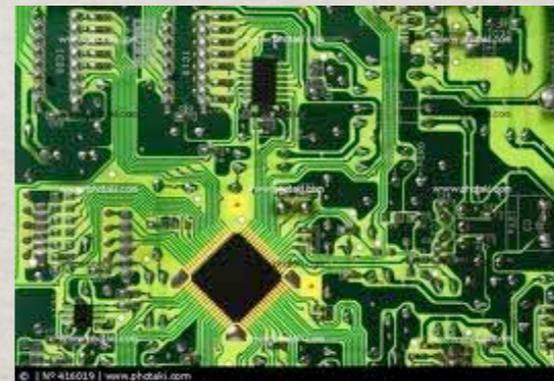
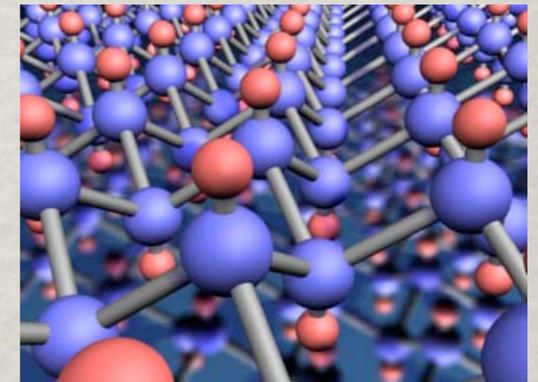
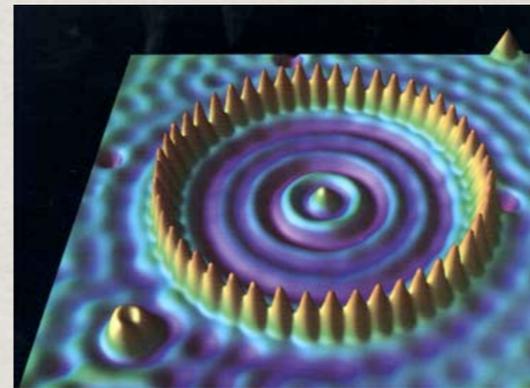
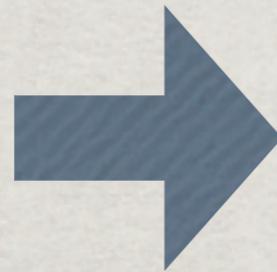
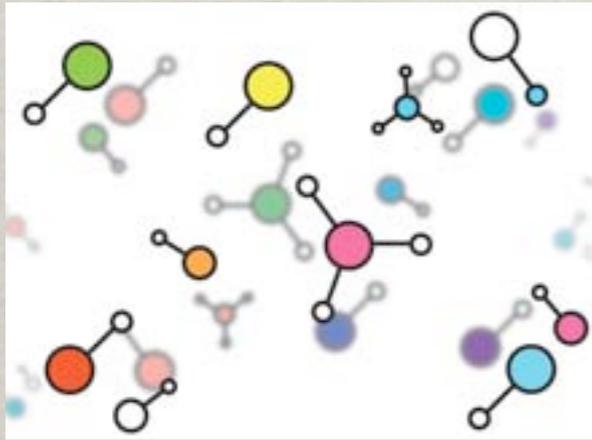


**Chao Yang**  
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FASTMath Institute\*

**Collaborations with FASTMath\* and SUPER SciDAC Institutes**

**The objective of our proposed work is to develop and implement new methods and theories to predict electronic excited state phenomena in energy related materials, e.g., materials for photovoltaics, photocatalysis, and electrical energy storage.**

# Use the underlying laws of quantum theory to predict and design materials

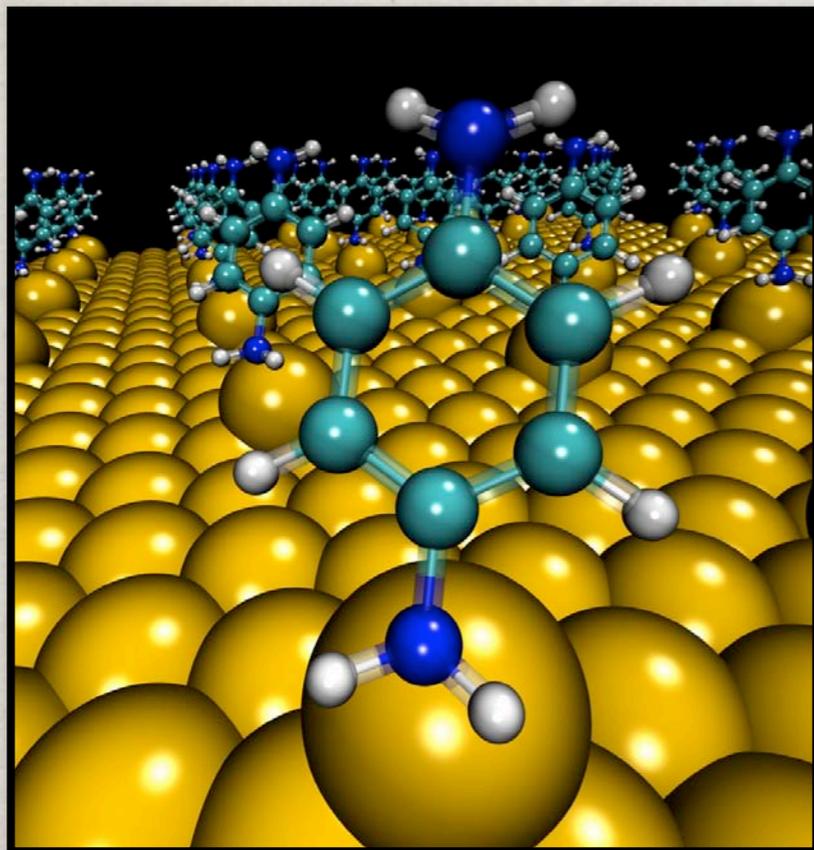


From atoms to solar cells, electronic devices, biomolecular systems, catalysts...

# Science Applications

- **Chromophore or dye molecules in gas-phase, in solution, or at an oxide surface**
- **Solvents, e.g. water or electrolyte, in contact with an oxide or metal electrode**
- **Molecular junctions and self-assembled monolayers**
- **Multicomponent inorganic semiconductor nanostructures**
- **Transition metal oxides, with defects, dopants, and with magnetic cations**
- **Nanophase crystals and clusters appropriate for photovoltaic applications**
- **Organic molecular crystals and assemblies, and donor-acceptor molecular interfaces**

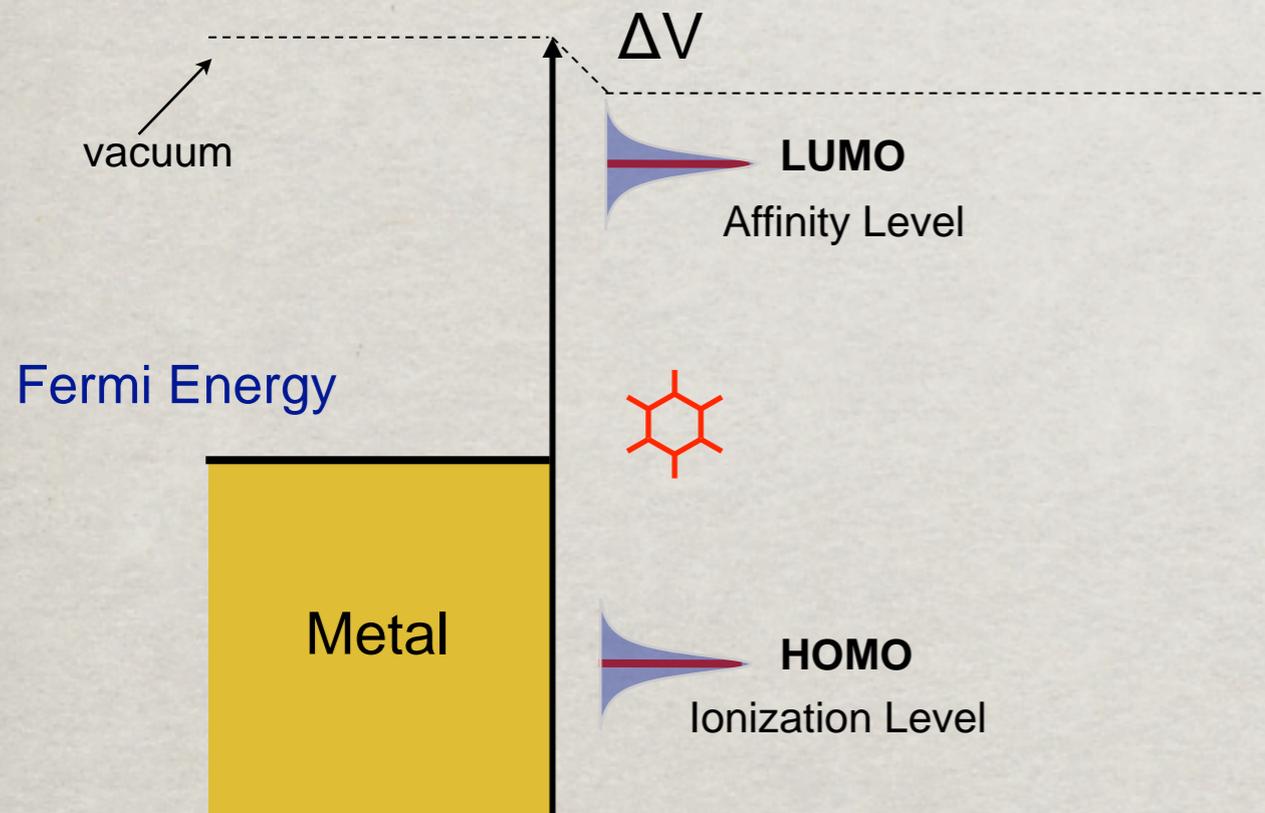
# Example: Electronic Structure of Organic-Inorganic Interfaces



- Organics are prevalent in next-generation energy conversion technology
- Energy conversion efficiencies are controlled in part by charge transfer and transport at interfaces
- Need for quantitative theory of structure and electronic energy level alignment of inorganic-organic interfaces

# Level alignment at metal-molecule contacts

Energy level diagram



## Physical effects influencing level alignment

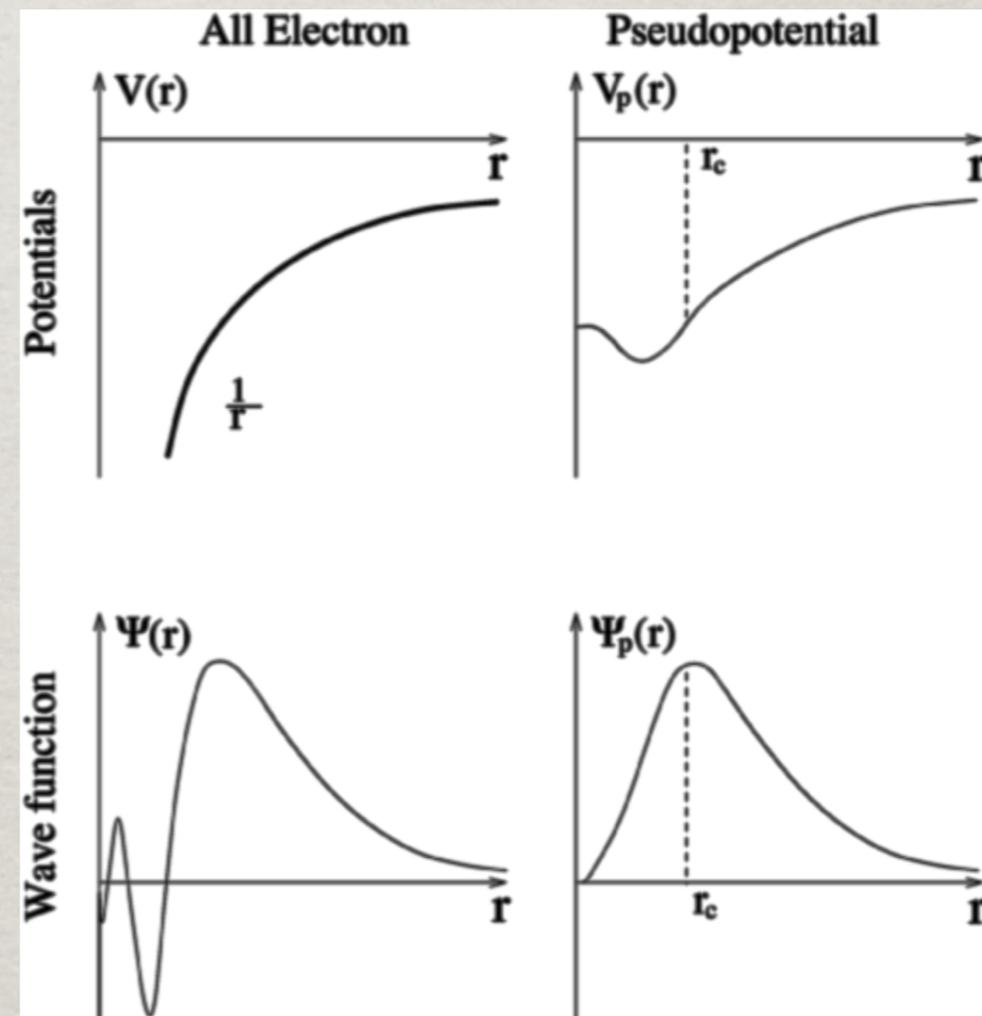
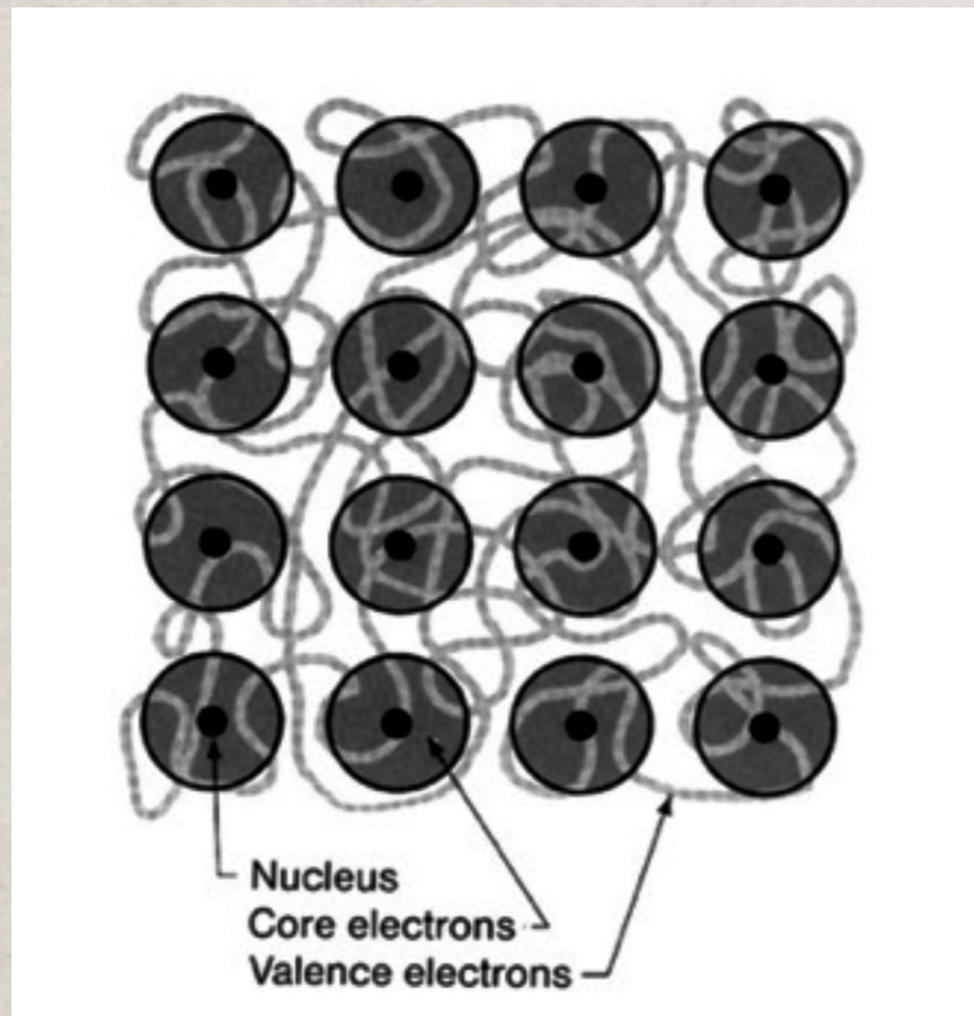
- IP and work functions
- Interfacial charge transfer: Induced interface dipole  $\Delta V \sim \Delta p/A$
- Energy level broadening: Hybridization, lifetime
- Surface polarization: Non-local “image charge” effects

# **The Ground State**

**Imperative to know the structural properties of materials and to establish an underlying description of the electronic structure problem.**

# Pseudopotential Theory

Focus on chemically active electronic (valence) states. Capture the physical content of the periodic table. Sets the energy and length scale to the chemically relevant states.



# Density Functional Theory

**Solving the Kohn-Sham Problem:**

$$\left[ -\frac{\hbar^2 \nabla^2}{2m} + V_{ion}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r}) \right] \psi_n(\vec{r}) = E_n \psi_n(\vec{r})$$

**Hartree-Potential**

$$V_H(\vec{r}) = e \int \frac{\rho(\vec{r}')}{|\vec{r}' - \vec{r}|} d^3 r'$$

**Charge density**

$$\rho(\vec{r}) = e \sum_{occup} |\psi_n(\vec{r})|^2$$

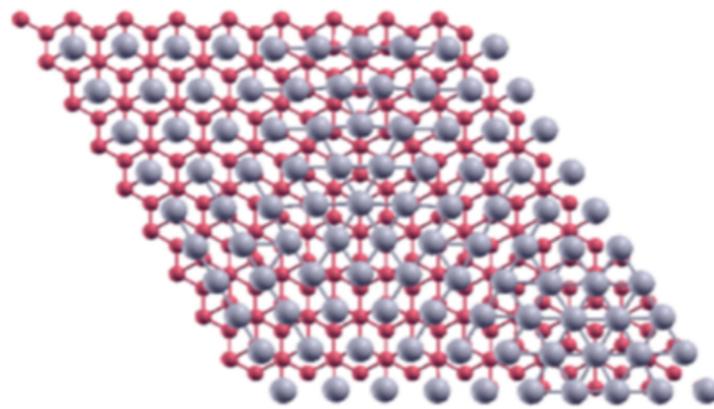
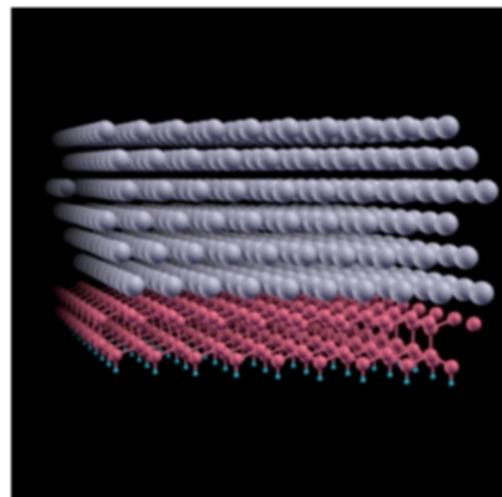
**Effective many body potential**

$$V_{xc}(\vec{r}) = V_{xc}[\rho(\vec{r})]$$

# Electronic energy from a solution to the Kohn-Sham Problem

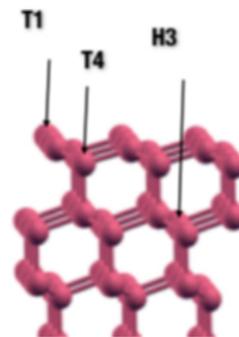
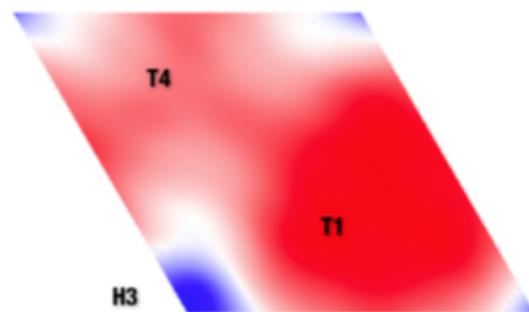
$$E_{Total} = \frac{1}{2} \sum_{i,j;i \neq j} \frac{Z_i Z_j e^2}{|\vec{R}_i - \vec{R}_j|} + E_{electronic}$$

$$E_{electronic} = \sum_{n,occup} E_n - \frac{1}{2} \int d^3r V_H \rho + \int d^3r [\epsilon_{xc} - V_{xc}] \rho$$



Scale:  $\Delta h$

Blue	+0.0000
Light Blue	+0.0087
White	+0.0173
Light Red	+0.0260
Red	+0.0346
Dark Red	+0.0433



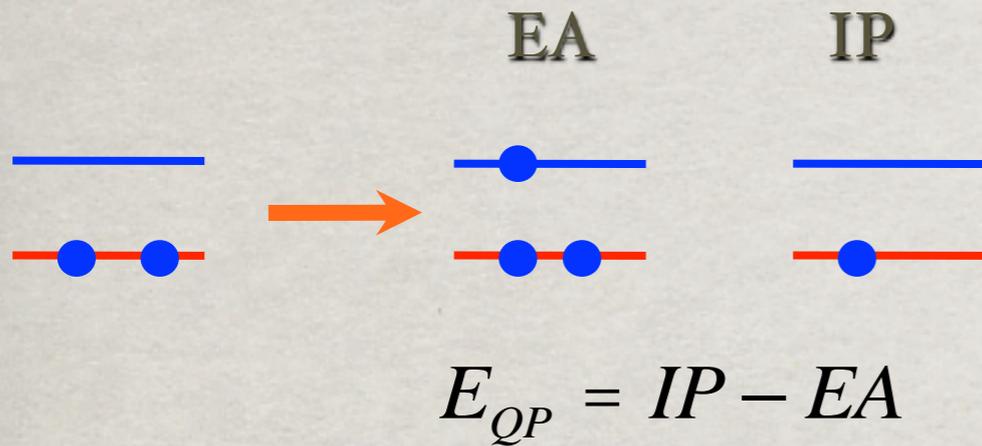
**Example: Understanding the structure of a metal-semiconductor interface (Pb on Si). Lattice mismatch has 10 Pb atoms for every 9 Si atoms.**

**1500 atoms were treated and the structure was fully relaxed.**

# **The Excited State**

**Imperative to know the electronic and optical properties of materials for a variety of energy related applications.**

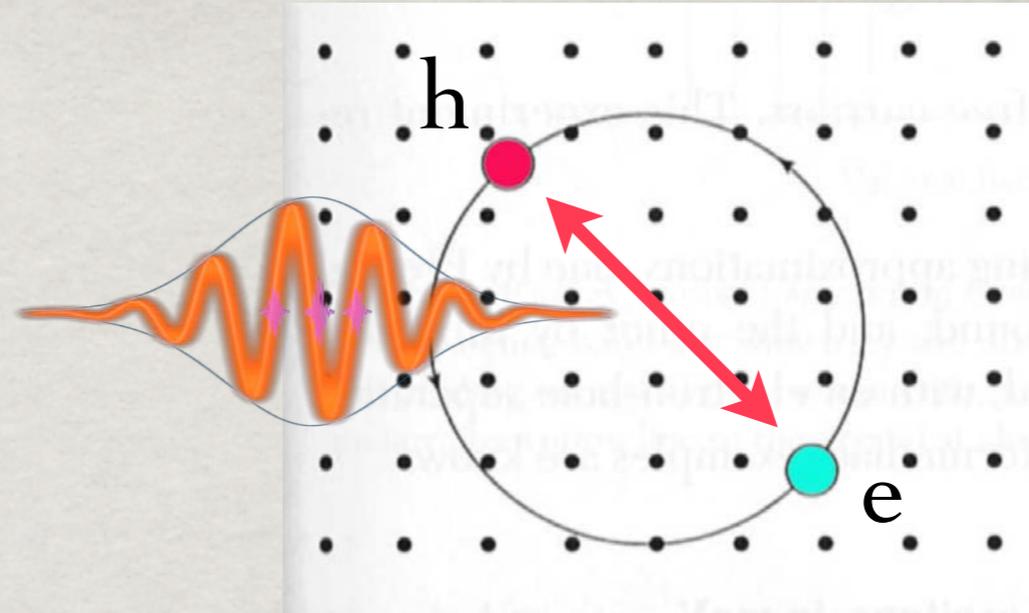
# Nomenclature:



**EA=Energy to add an electron  
(Electron affinity)**

**IP=Energy to remove an electron  
(Ionization potential)**

**Quasiparticle band gap=IP-EA**

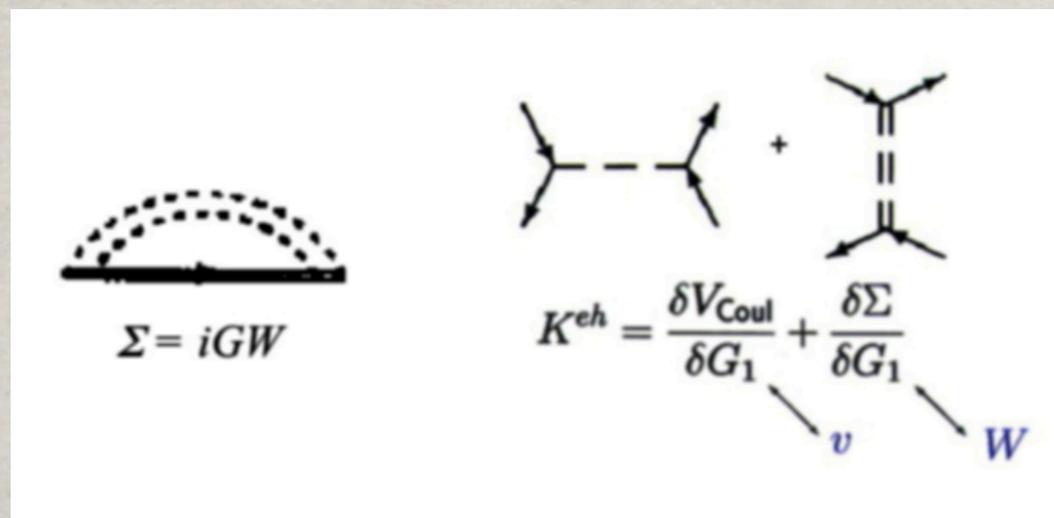


**Light absorbed by a solid creates  
an electron-hole pair**



**Interacting electron-hole pair are **excitons****  
**“Optical gap” is the energy to create an exciton state**

**This is a many body problem wherein  
optical excitations can be coupled to  
structural changes.**



# Quasiparticle Energies: The GW Method

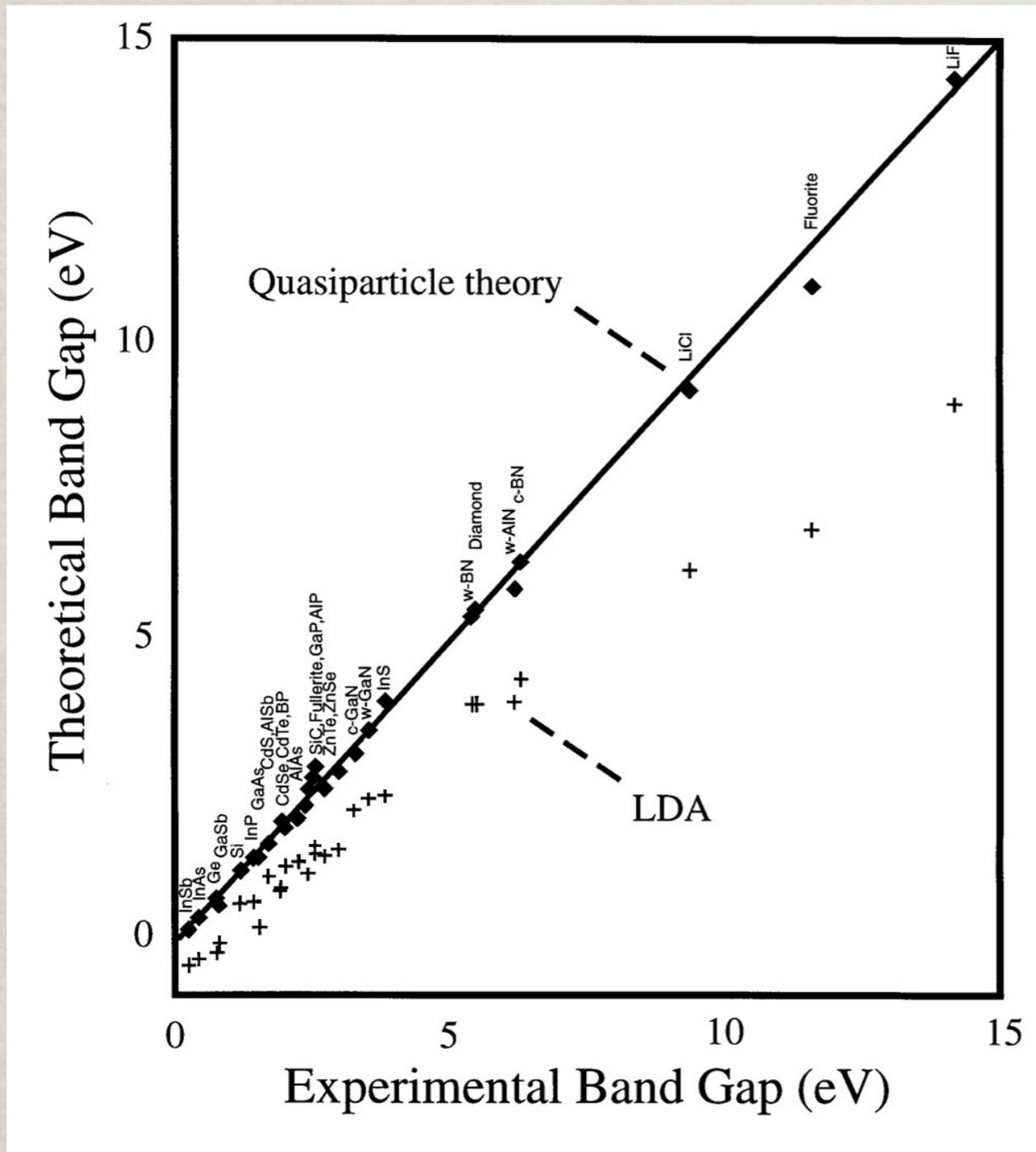
$$\left[ -\frac{1}{2} \nabla^2 + V_{\text{ion}} + V_{\text{H}} + \Sigma(E_n^{\text{QP}}) \right] \psi_n^{\text{QP}} = E_n^{\text{QP}} \psi_n^{\text{QP}}$$

The quasiparticle energy corresponds to the energy create to particle-like excitation in a system, e.g., adding a particle to or removing a particle from a system of N interacting particles.

$$\Sigma(\mathbf{r}, \mathbf{r}', \omega) = i \int \frac{dE'}{2\pi} e^{-i\delta\omega'} G(\mathbf{r}, \mathbf{r}'; \omega - \omega') W(\mathbf{r}, \mathbf{r}'; \omega')$$

$\Sigma$  is the non-local, energy-dependent, non-Hermitian, self-energy operator; its exact form is unknown, but progress can be made by approximating it within many-body perturbation theory, e.g., as the first term of an expansion in the screened Coulomb interaction.

# GW Method Yields Accurate Quasiparticle Gaps



**Example of GW calculations for “band gaps” of binary compounds.**

# The Bethe-Salpeter Equation

Building on the GW approximation for  $\Sigma$ , neutral (**electron-hole**) excitations, probed in optical or other measurements, can be calculated through the solution of a Bethe-Salpeter equation.

$$\left( E_{c\mathbf{k}}^{\text{QP}} - E_{v\mathbf{k}}^{\text{QP}} \right) A_{v\mathbf{k}}^S + \sum_{v'c'\mathbf{k}'} \langle v\mathbf{k} | K^{\text{eh}} | v'c'\mathbf{k}' \rangle = \Omega^S A_{v\mathbf{k}}^S$$

where  $|v\mathbf{k}\rangle$  is the product of occupied (denoted by index  $v$ ) and unoccupied ( $c$ ) quasiparticle states of the same wave vector  $\mathbf{k}$ . The electron-hole amplitude or exciton wave function can be expressed in real space as

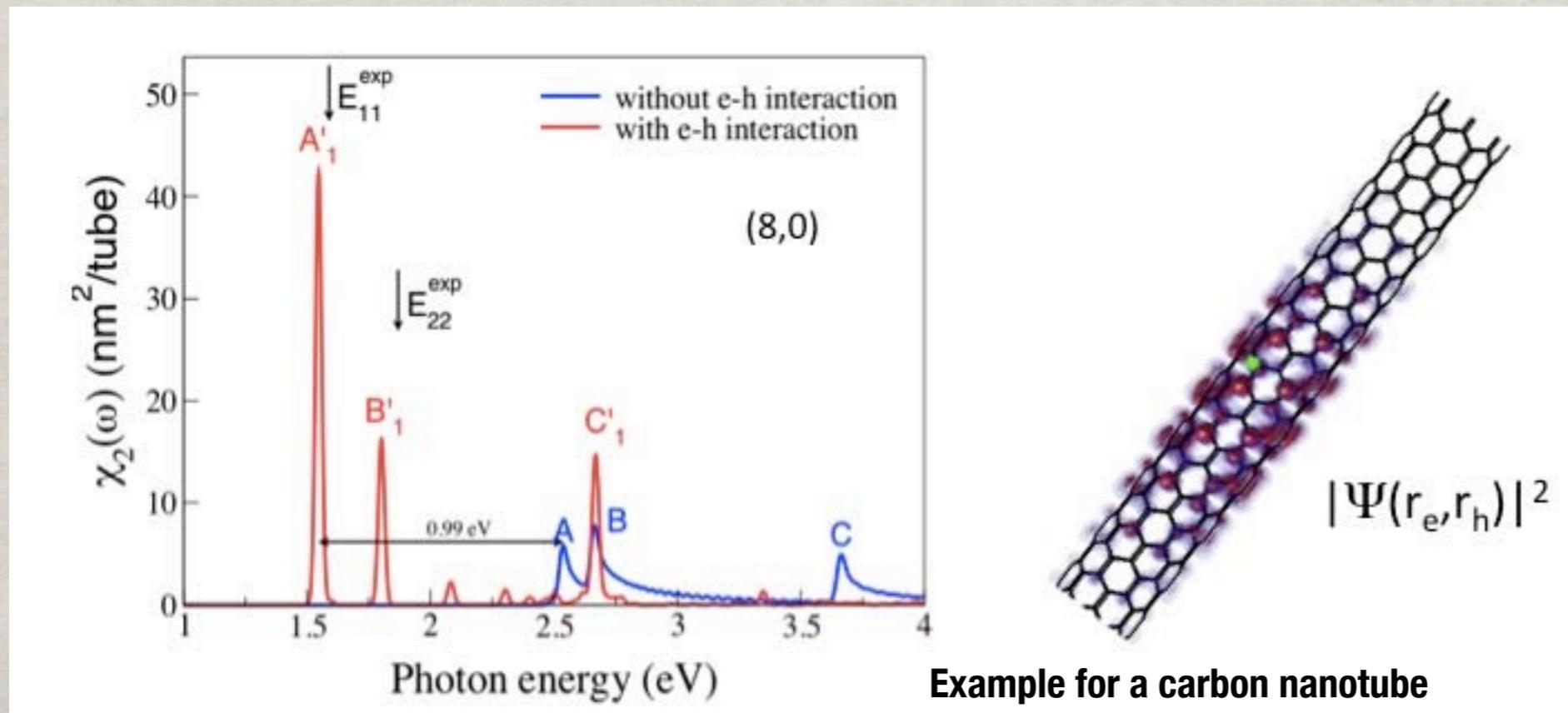
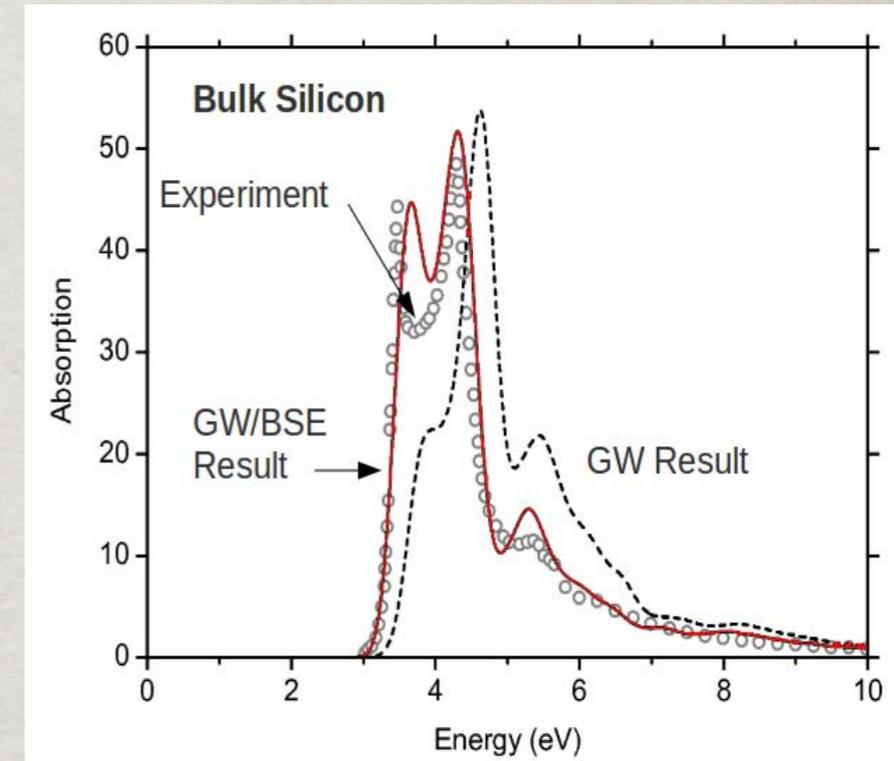
$$\Psi(\mathbf{r}_e, \mathbf{r}_h) = \sum_{\mathbf{k}c\nu} A_{\nu\mathbf{k}}^S \psi_{c\mathbf{k}}(\mathbf{r}_e) \psi_{\nu\mathbf{k}}^*(\mathbf{r}_h)$$

Optical absorption spectra can be obtained from the imaginary part of the transverse dielectric function, which can be written:

$$\epsilon_2(\omega) = \frac{16\pi^2 e^2}{\omega^2} \sum_S |\mathbf{e} \cdot \langle 0 | \mathbf{v} | S \rangle|^2 \delta(\omega - \Omega^S)$$

$$\langle 0 | \mathbf{v} | S \rangle = \sum_{v\mathbf{k}} A^S \langle v\mathbf{k} | \mathbf{v} | c\mathbf{k} \rangle$$

and  $\mathbf{v}$  is the velocity operator along the direction of the polarization of light,  $\mathbf{e}$ .



Example for a carbon nanotube

# **Computational Issues: Ground State**

- Numerous degrees of freedom: Many body problem**
- Requires a very precise algorithm**
- Problem scales poorly: Typically the Kohn-Sham problem scales in a super linear fashion.**

**Key issue: Solving the an eigenvalue problem for large systems.**

**Status: Typically a few thousand atoms can be handled.**

# Computational Issues: Excited State

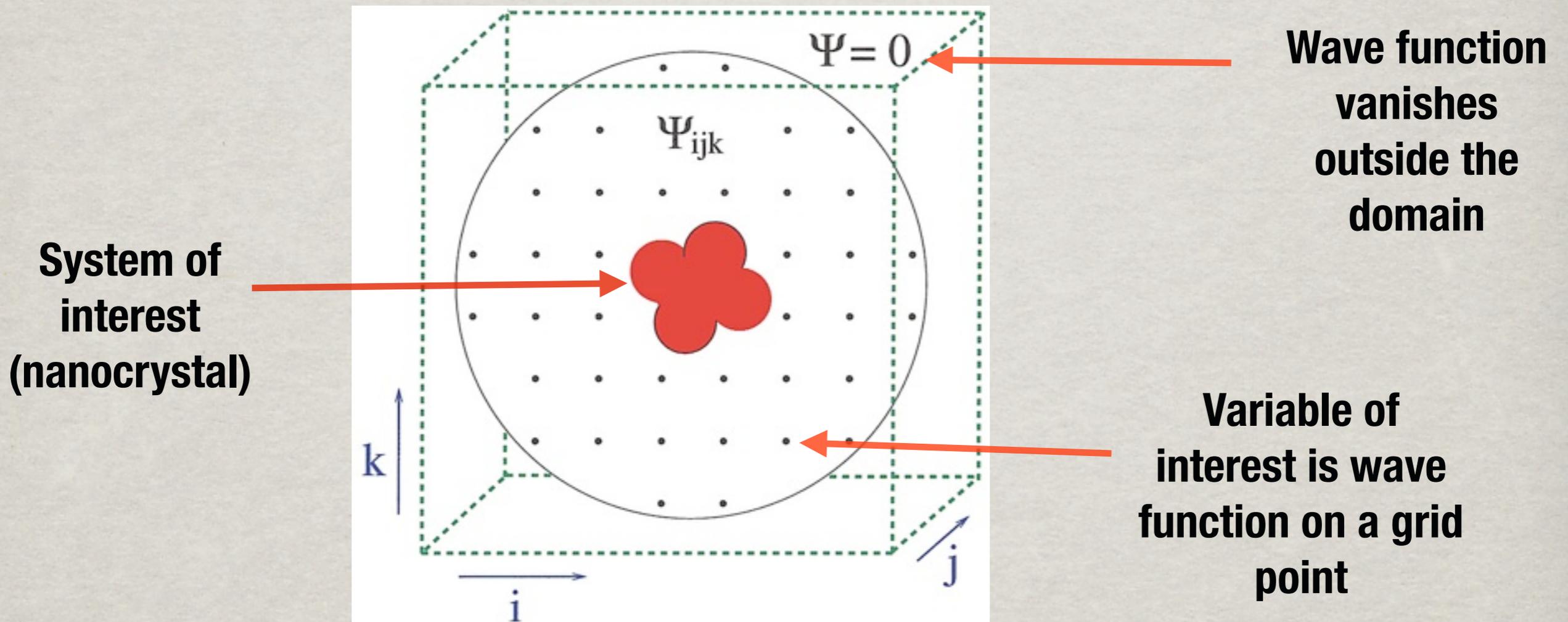
- **Numerous degrees of freedom: Many body problem**
- **Problem scales poorly: In principle, the Bethe-Salpeter equation scales as  $N^6$  where  $N$  is the number of atoms.**
- **Large number of unoccupied states considered.**
- **Semi-core states often need to be explicitly handled.**

**Key issue: Handling the empty state problem, improve scalability by numerical and hardware approaches, e.g., GPU's.**

**Status: Typically a hundred atoms can be handled.**

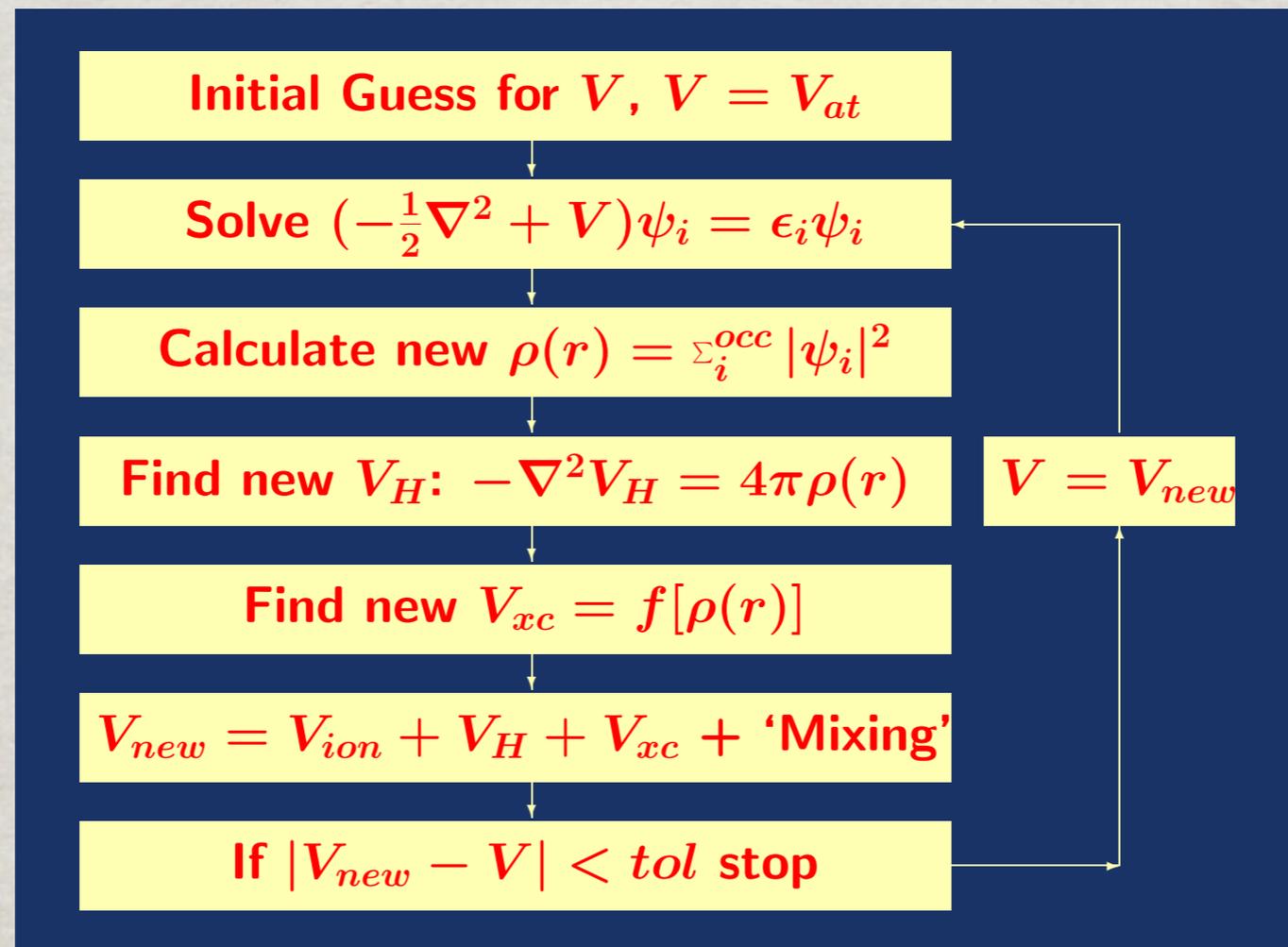
**Example: New algorithms for a “parallel eigensolver”**

# Solving the Kohn-Sham Problem in Real Space



**Discretize Kohn-Sham Equation:  
Solve using higher-order finite differencing**

# “Traditional Approach to the Kohn-Sham Problem”



Most of the time is spent on the diagonalization part.

One can use ARPACK, variant of the Lanczos process (Implicitly Restarted Lanczos)

# Filtered Subspace Iteration

Define charge density matrix:

$$P = \Phi^T \Phi \quad \Phi = [\psi_1, \psi_2, \dots, \psi_{occup}]$$

where the diagonal is the charge density.

For any orthonormal matrix  $U$ , we can write

$$P = \Phi^T (U^T U) \Phi = (\Phi U)^T (U \Phi)$$

We do not need explicit vectors, we only need to know

$$U\Phi$$

We can find this using subspace filtering.

# Nature of the Filter

Given the diagonalized solution:

Let us consider a polynomial filter,  $p(H)$

$$H = Q^T \Lambda Q \quad \Lambda = \text{diag}(\lambda_1, \lambda_2, \dots, \lambda_N) \quad Q = [\psi_1, \psi_2, \dots, \psi_N]$$

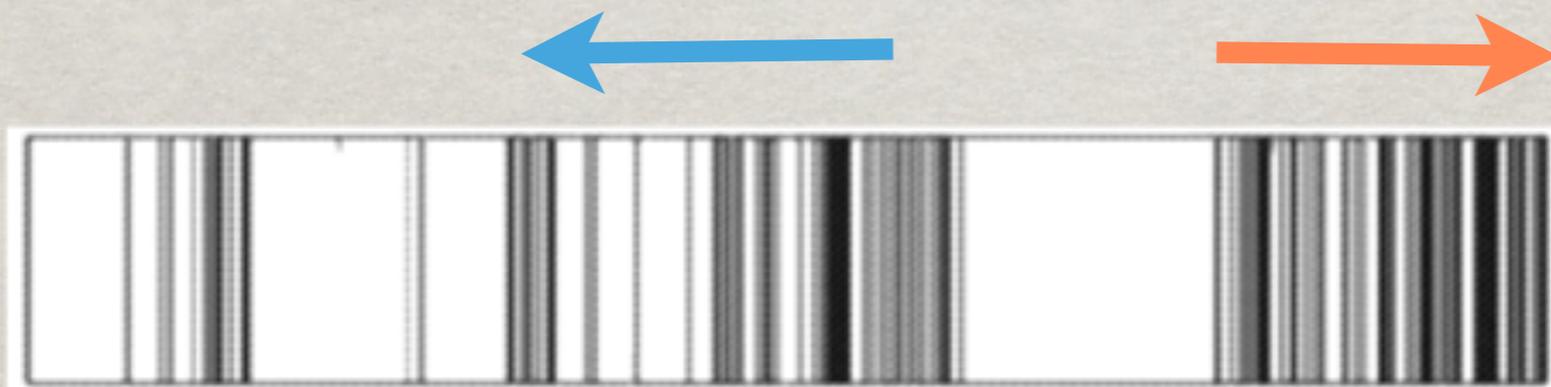
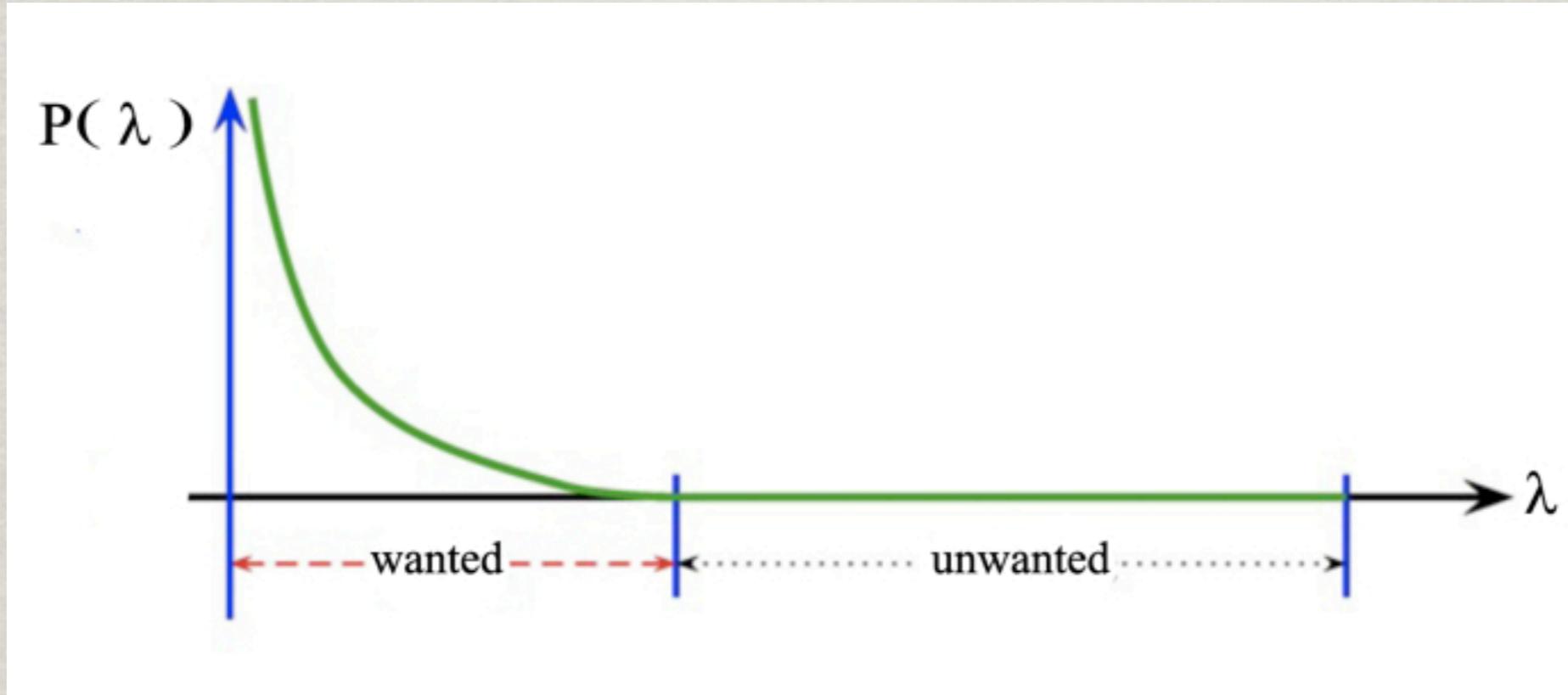
$$P(H) = Q^T P(\Lambda) Q = \sum_{i=1}^N P(\lambda_i) \psi_i^T \psi_i$$

$$P(H)v = \sum_{i=1}^N P(\lambda_i) (\psi_i^T v) \psi_i$$

Suppose we choose our filter such that it is small for states not of interest, e.g.,  $p \approx 0$ , for empty states, then we can approach what we want

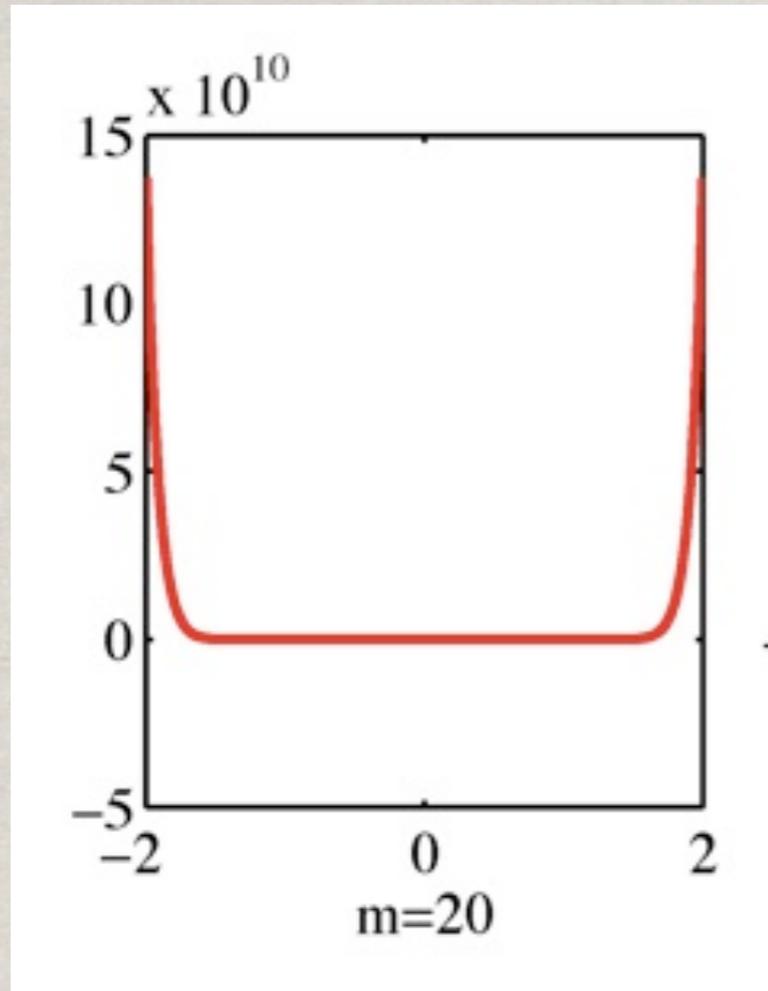
$$\hat{\psi}_j = P(H)v_j = \sum_{\text{occup}} P(\lambda_i) (\psi_i^T v_j) \psi_i \quad \Rightarrow \quad \hat{\psi} = U \psi$$

**Qualitatively we want a polynomial that looks like this:**



**Enhanced**

**Suppressed**



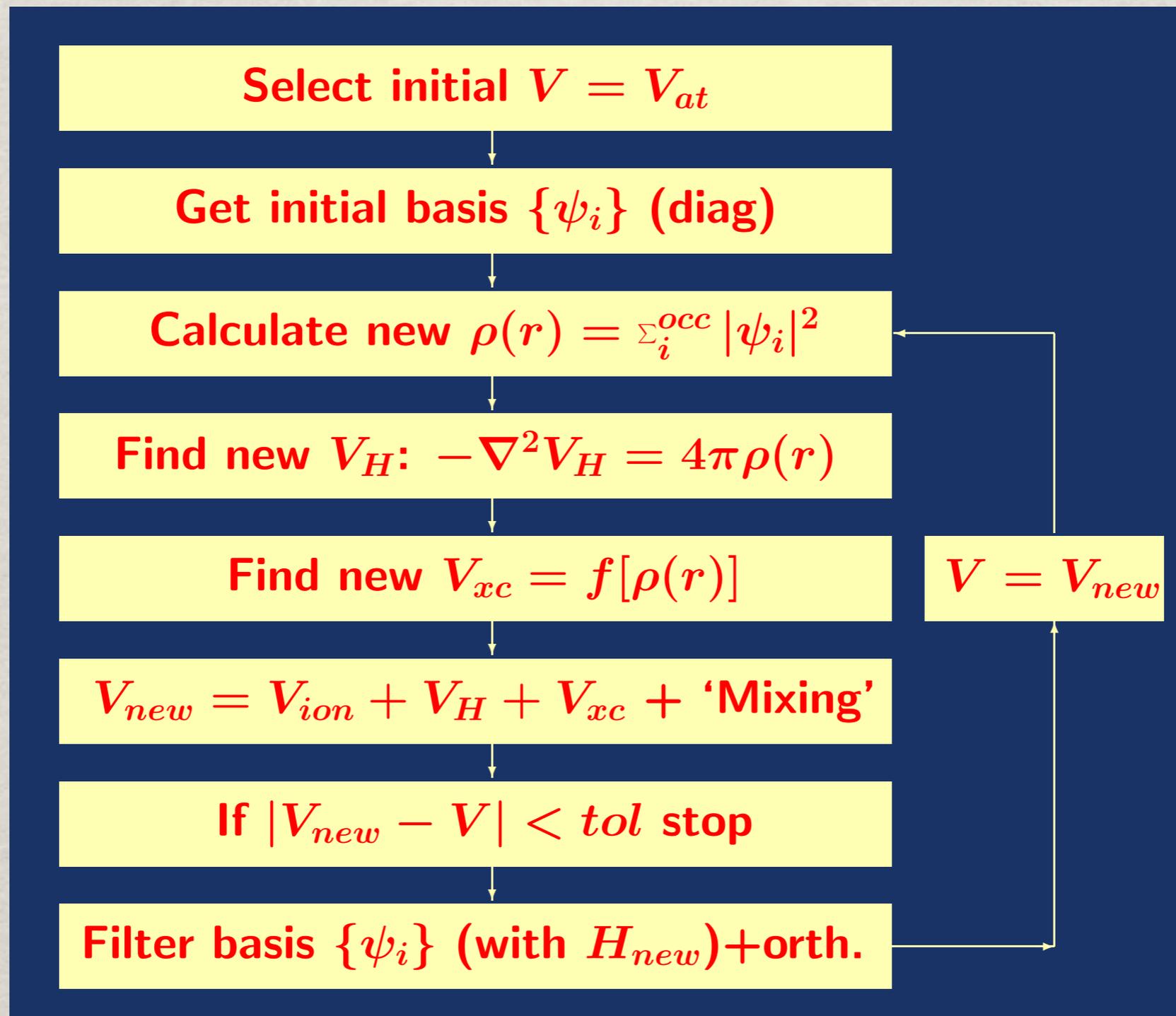
**Example of Chebyshev polynomial with  $m=20$**

**Chebyshev  
Polynomials:**

$$P_0 = 1 \quad P_1 = x \quad P_{n+1} = 2xP_n - P_{n-1}$$

**This polynomials grow rapidly outside of the interval  $[-1,1]$   
and have a convenient recursion relationship.**

# “Non-Traditional Approach to the Kohn-Sham Problem”



**Filtering operation replaces diagonalization operation.**

# “Typical Results”

method	# MV products	# SCF	total_eV /atom	CPU(secs)
CheFSI	124761	11	-77.316873	5946.69
ARPACK	142047	10	-77.316873	62026.37
TRLan	145909	10	-77.316873	26852.84

$Si_{525}H_{276}$ ,  $N = 292584$ ,  $n_{occ} = 1194$ ,  $m = 8$ .

ARPACK: Implicit restart Arnoldi/Lanczos code, one of the best public domain eigenvalue packages, often used for benchmarking. (R. Lehoucq, D. Sorensen, C. Yang).

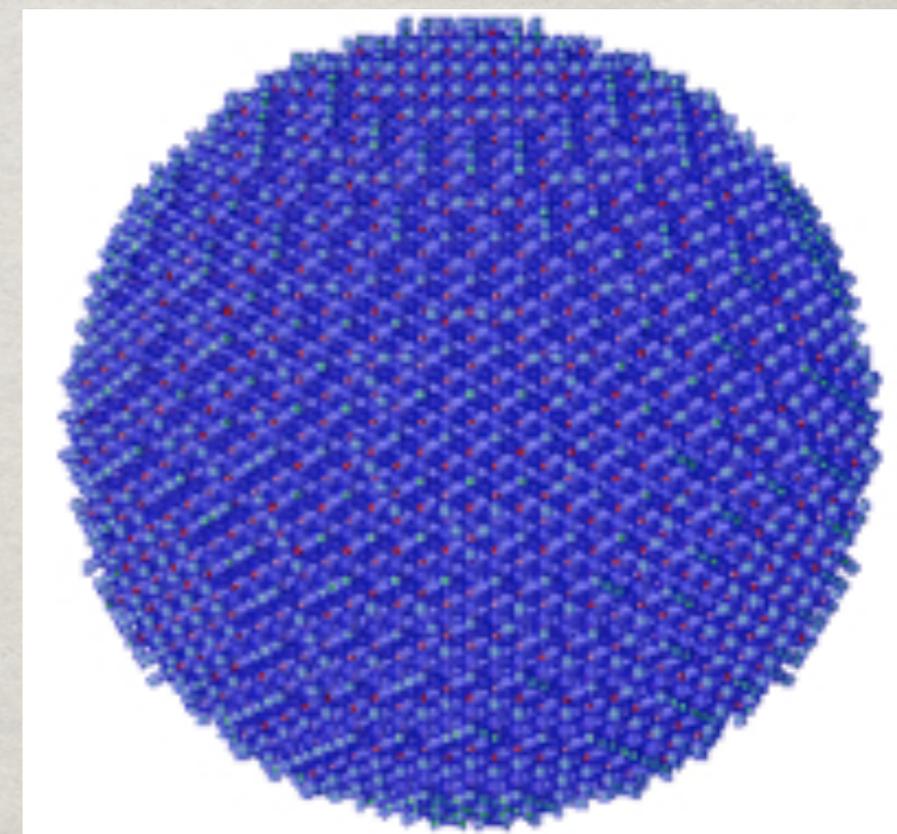
TRLan: Thick-restart Lanczos. (K. Wu, H. Simon).  
(improved symmetric eigensolver based on ARPACK).

**Note: This is not an approximate method.**

**[HTTP://PARSEC.ICES.UTEXAS.EDU](http://parsec.ices.utexas.edu)**

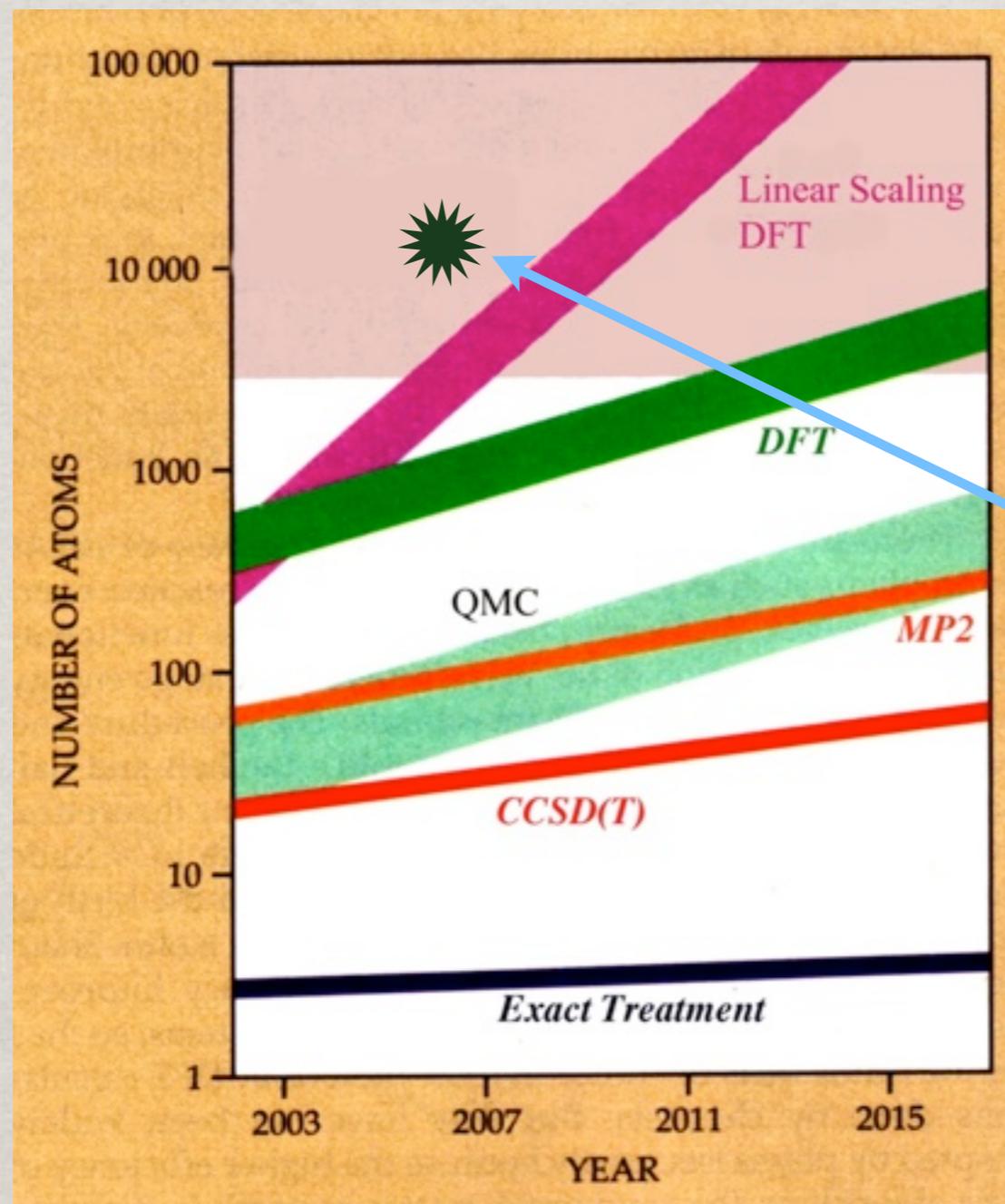
**Phys. Rev. E 74, 066704 (2006)**

**Largest system to date**



**$Si_{904I}H_{1860}$   
diameter = 7 nm**

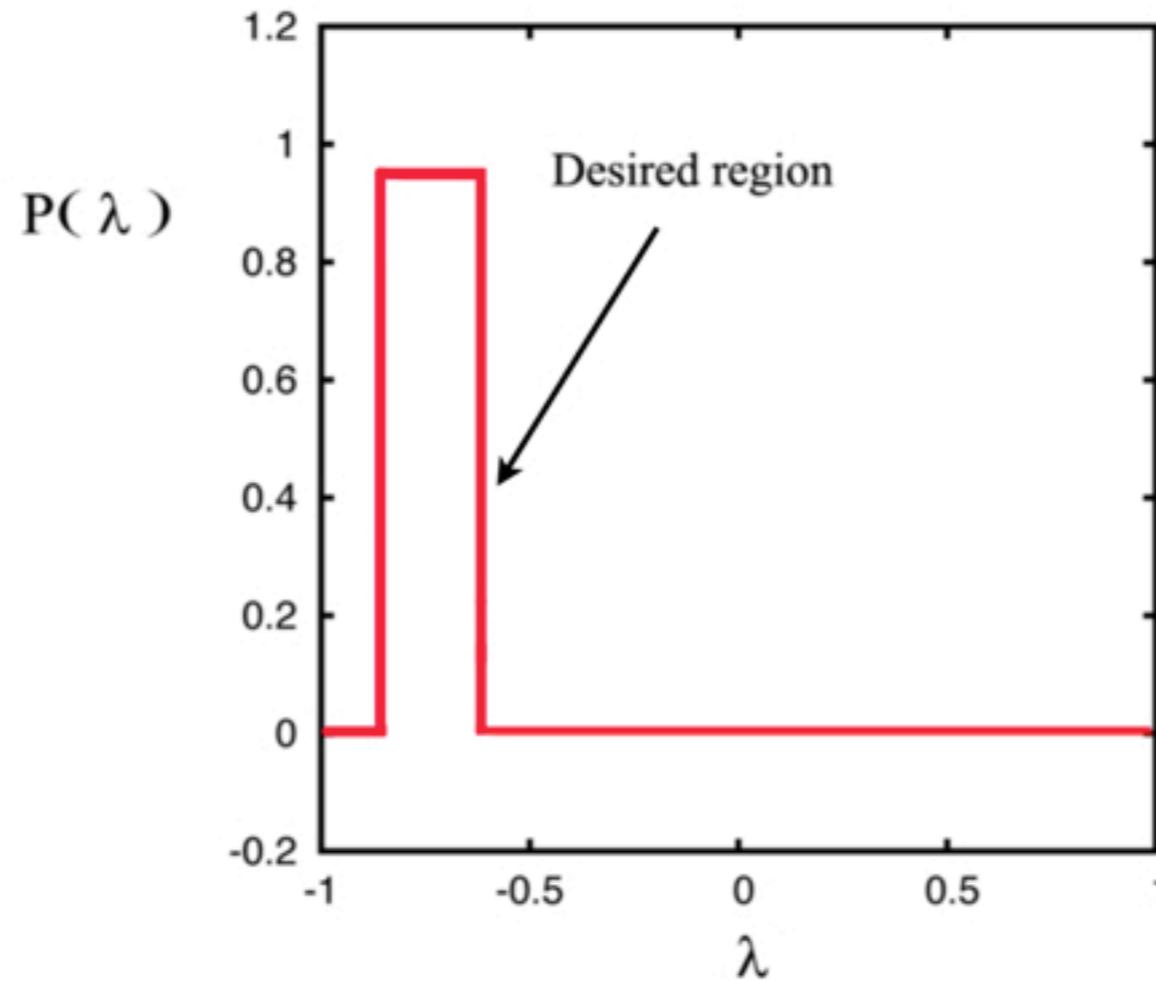
# “Time to solution” (TTS) Figure of Merit



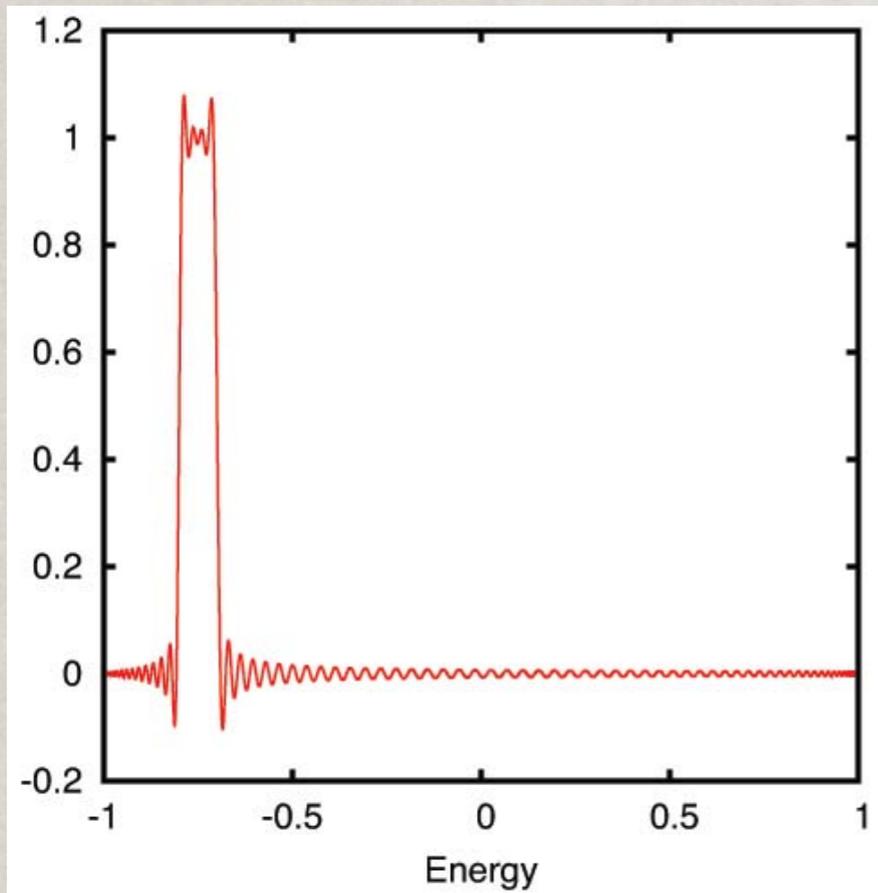
Results for  
**Si<sub>9041</sub>H<sub>1860</sub>**

M. Head-Gordon and E. Artacho, *Physics Today* (2008).

# The Future



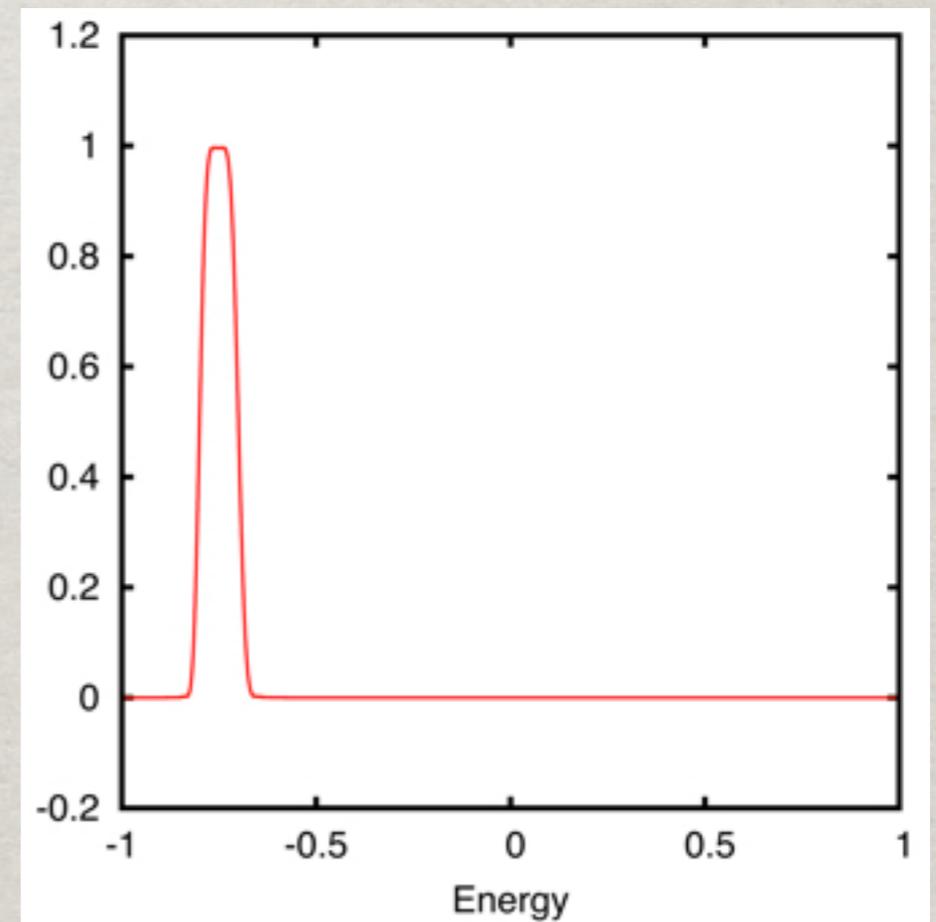
**Suppose we choose our filter for just a part of the spectrum?**



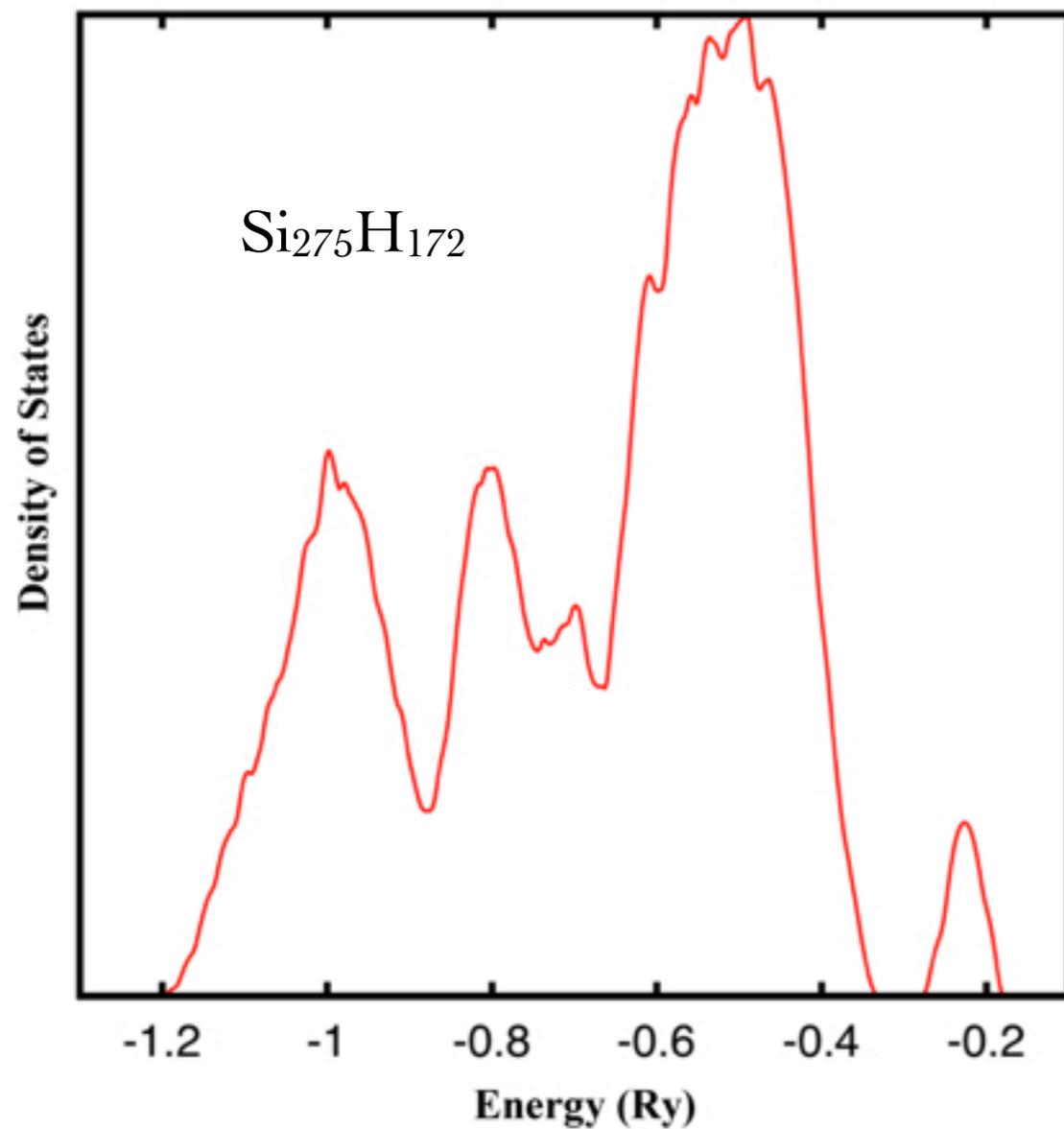
**Expressing step function with Chebyshev polynomials is an issue. Resulting window “rings.”**

**Chebyshev polynomials can be modified. “Chebyshev-Jackson” approximation shown at right.**

$$f(x) \approx \sum_{i=0}^k c_i g_i^k P_i(x)$$



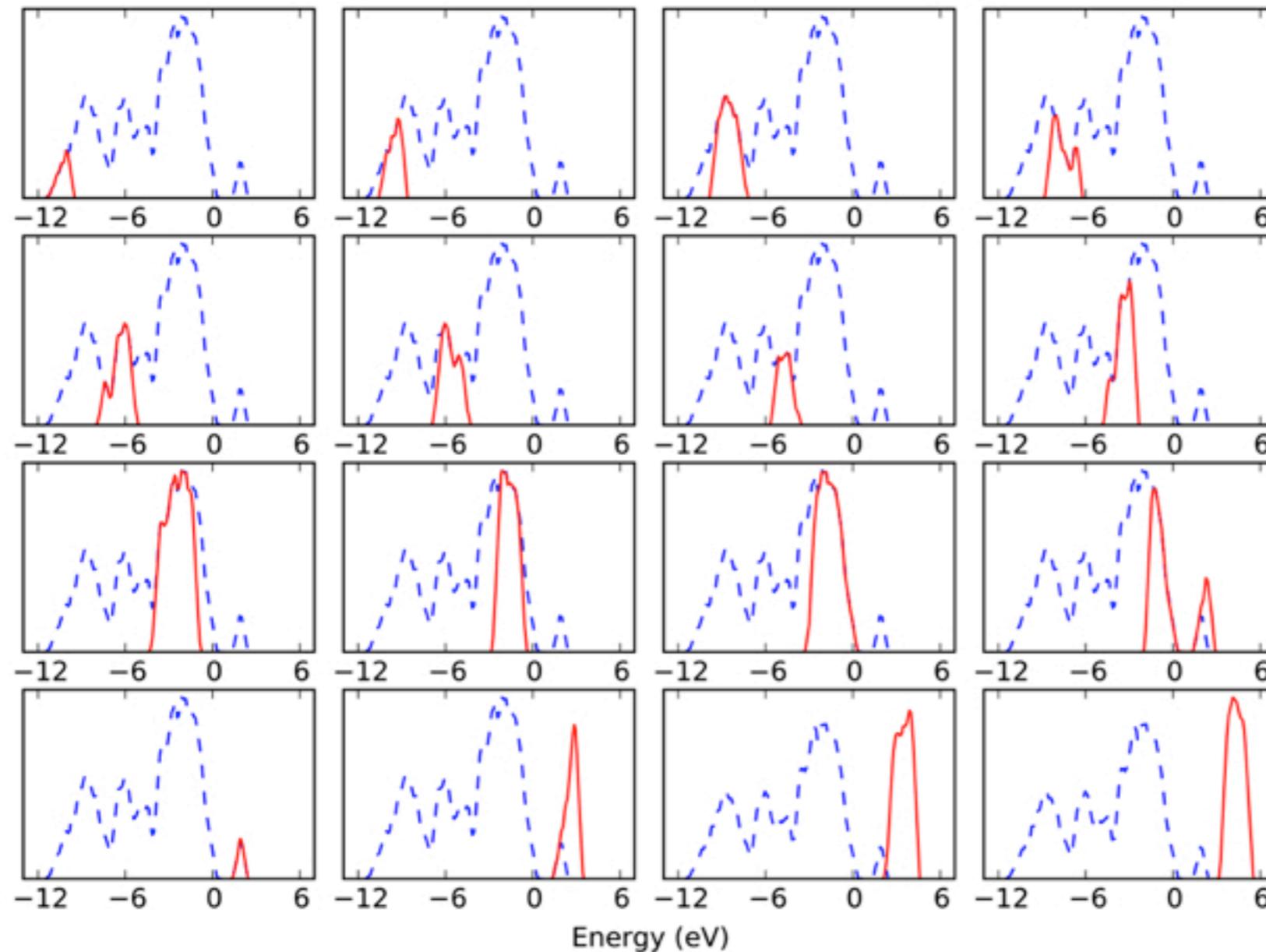
**Target: Eigenvalue  
spectrum (density of states)  
for Si quantum dot**



**Issues:**

- **Balance windows to contain similar number of eigenvalues**
- **Avoid missing eigenvalues**
- **Avoid double counting eigenvalues**

# Proof in Principle: Eigenvalue spectrum (density of states) for Si quantum dot calculated from 16 windows



**Spectrum agrees with “traditional” calculations.**

**Each window done independently.**

**Schofield, Chelikowsky and Saad, Computer Physics Communications 183, 497 (2012)**

# Deliverables

- **Massively-parallel, open-source code spanning both ground and excited state properties code will support mixed shared and distributed memory models as well as mixed CPU and GPU machines**
  - ➔ **Capable of handling large systems of energy relevant materials with a variety of boundary conditions**
  - ➔ **Well-interfaced to commonly accessible electronic structure codes in the materials research community and available on the web**

# Milestones

- **Complete work on “parallel eigensolver.” Optimize GW/BSE code to incorporate empty state formalism. Develop seamless interface between ground state and excited state codes\*.**
- **Extend GW/BSE codes to systems with thousand of atoms.**

**\*Codes will be developed and optimized to target the DOE machines at NERSC and the LCF machines at Oak Ridge and Argonne National Labs.**