WAVEFUNCTIONS WITH ABSORPTIVE BOUNDARY CONDITIONS

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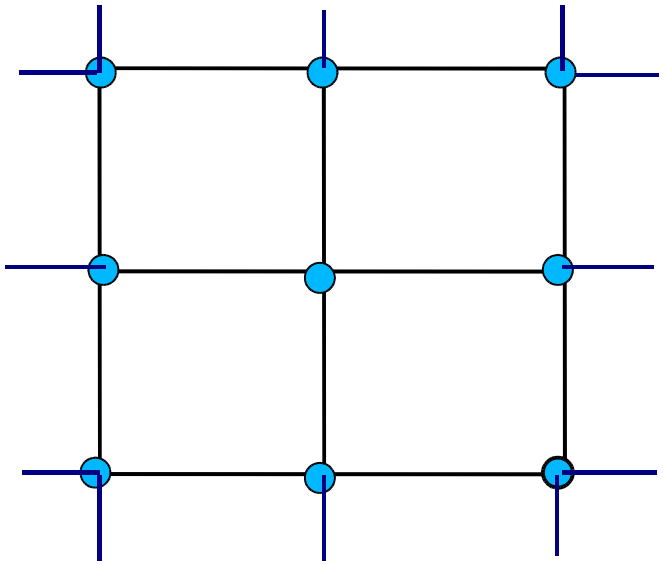
Problem: How to get the best electronic structure with the least calculation?

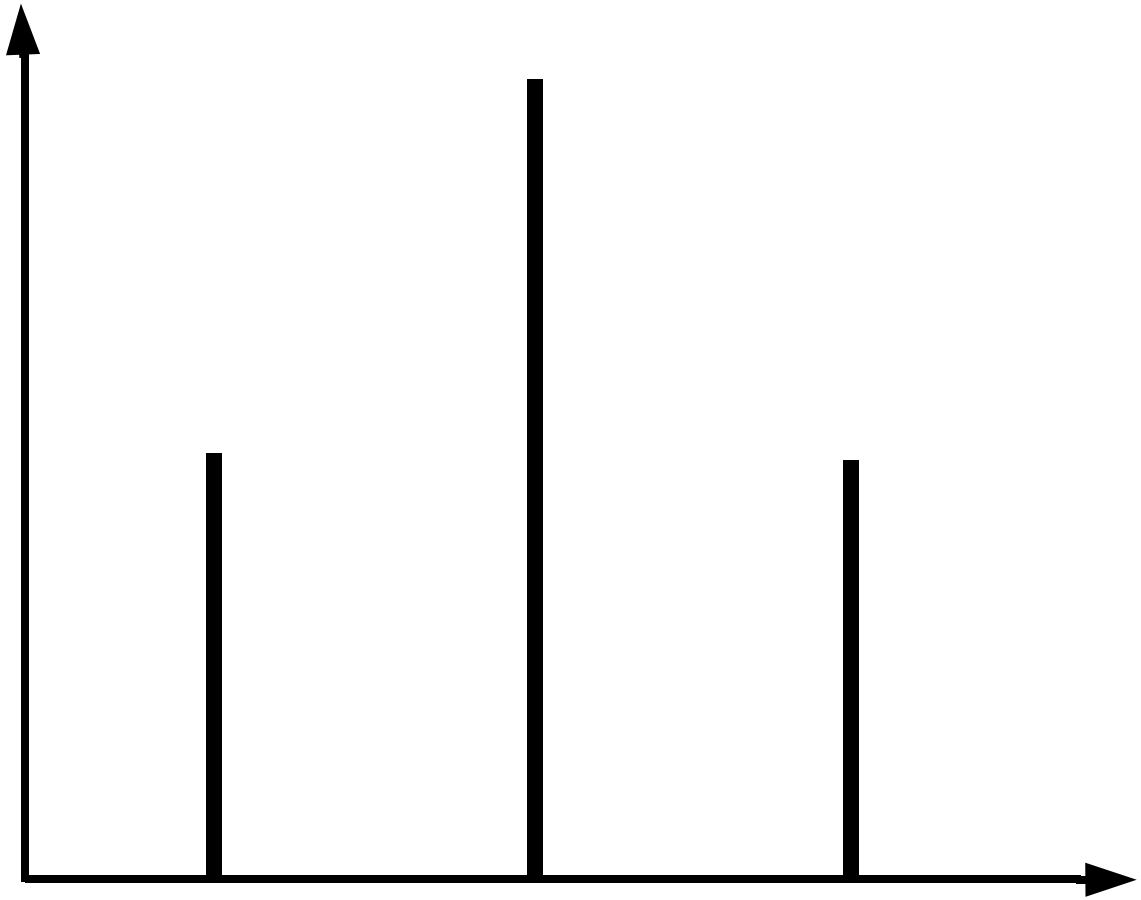
Solution: Do the calculation on a cluster with appropriate boundary conditions.

Problem: What boundary conditions?

Cluster Boundary Conditions



Projected Density of States



Highly singular density of states!

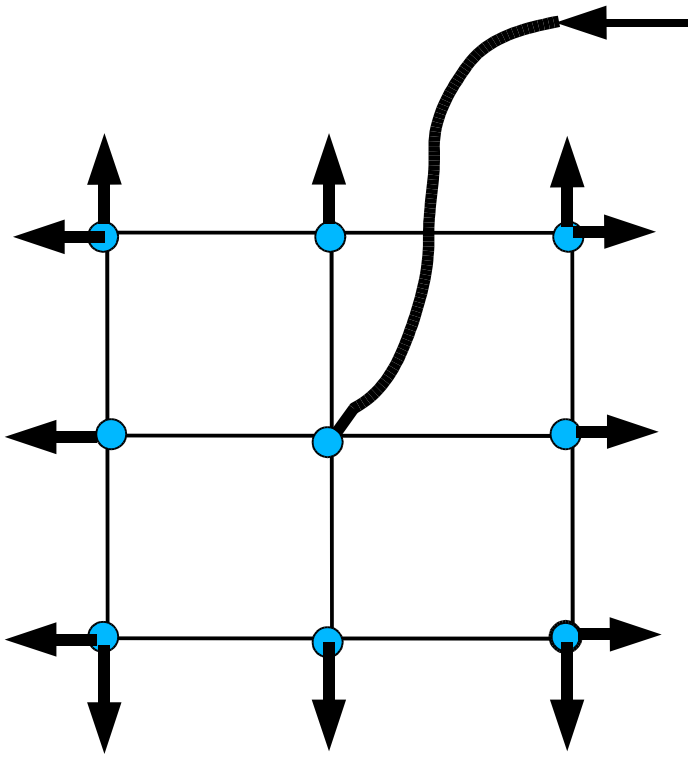
Interference between reflected waves causes oscillations in the density of states.

A smooth density of states comes from traveling waves – no reflections.

There are boundary conditions for the cluster which are exact for the infinite system, we just don't know what they are.

Like impedance matching to eliminate standing waves in transmission lines, maximize the power transmitted J while minimizing the total intensity I -

absorptive boundary conditions.

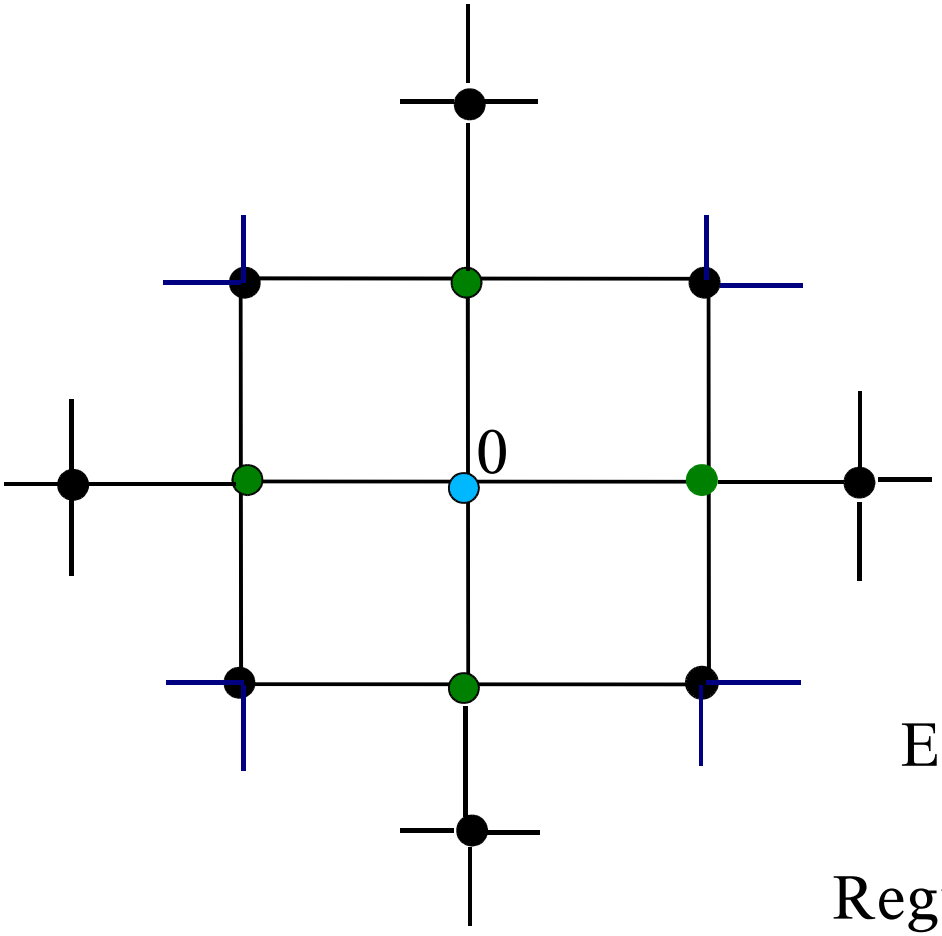


Insert current J though a lead attached to the central atom and extract it on the boundary.

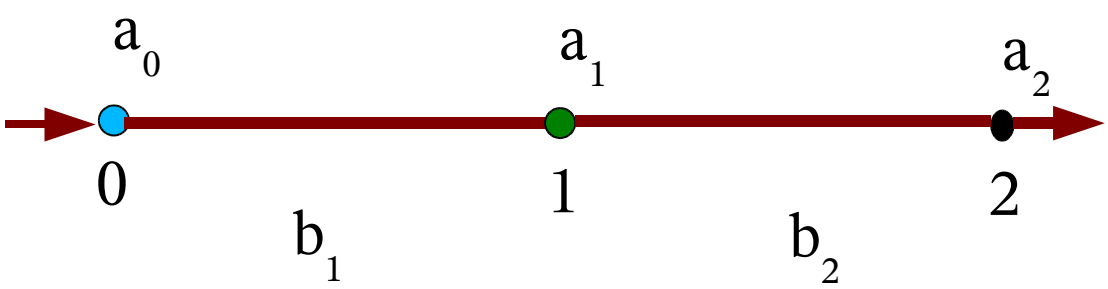
The intensity I is the sum of the probabilities of finding the electron on the atoms in the cluster.

Reflections increase I and decrease J.

Implementation



Tridiagonalize the cluster.



Construct two independent solutions to the Schrödinger Equation.

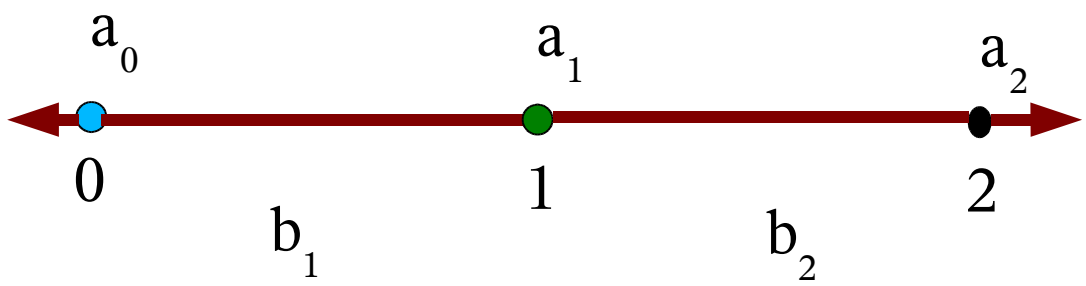
$$E\,\psi_n(E) = a_n\,\psi_n(E) + b_{n+1}\psi_{n+1}(E) + b_n\,\psi_{n-1}(E)$$

Regular solution: $b_0\,p_{-1}(E) = 0,\ \ p_0(E) = 1;$

Irregular solution: $b_0\,q_{-1}(E) = -1,\ \ q_0(E) = 0;$

General solution: $\psi_n(E) = p_n(E) + (u(E) + i\,v(E))\,q_n(E).$

There are u(E) and v(E) which are exact, but unknown.



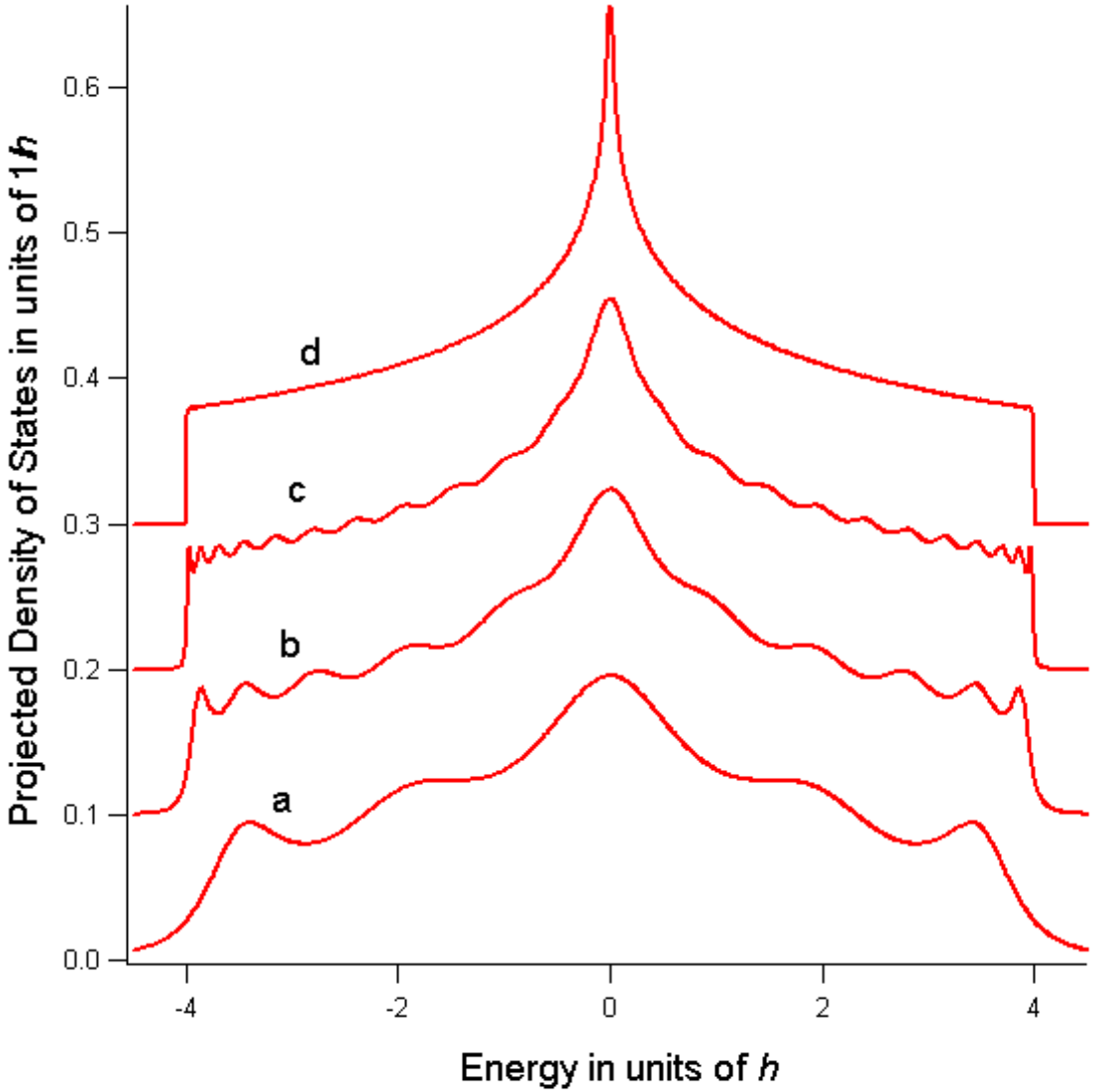
Current: $J = b_{n+1} [\psi_n(E)^* \psi_{n+1}(E) - \psi_{n+1}(E)^* \psi_n(E)] /2i$

Total intensity: $I = \Sigma \psi_n(E)^* \psi_n(E)$

For each E, vary u(E) and v(E) to minimize I while holding J constant (positive).

Projected Resolvent: $R(E) = \psi_0(E) /b_0 \psi_{-1}(E) = -1 /[u(E) + i\, v(E)]$

Projected density of states: $n(E) = [v(E) /\pi] /[u(E)^2 + v(E)^2]$



a) 5 levels
b) 11 levels
c) 25 levels
d) 199 levels

Figure 3.

Summary

- Smooth densities of states come from traveling waves – time-reversal doublets.
- Ideal traveling waves carry the maximum current with minimum intensity.
- At each energy the Schrödinger equation has at least two solutions which can be mixed to construct the best traveling wave and hence the best smooth density of states at that energy.