First-principles calculations of carrier scattering by substitutional carbon in silicon

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Overview

- First principles calculations for alloy scattering
  - General methodology
- Substitutional carbon in silicon
  - Motivation
  - Experimental mobilities
  - DFT calculations and application of model
  - Initial results
- Conclusions

First principles alloy scattering methodology

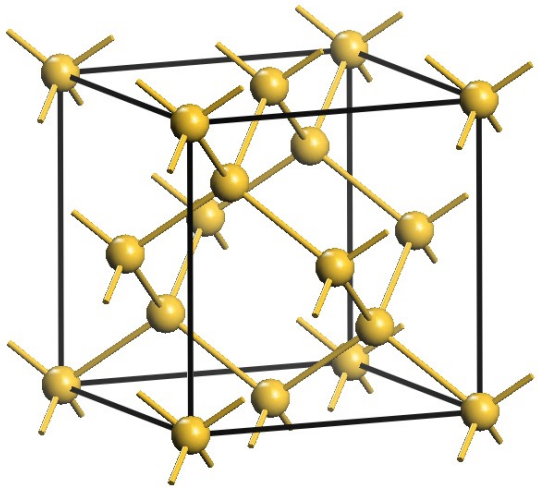
Method of calculating alloy scattering based on ab initio electronic structure calculations.

Previously used to calculate *n*-type [1,3] and *p*-type [2] alloy scattering in SiGe.

[1] F. Murphy-Armando and S. Fahy, *Phys. Rev. Lett*, **97**, 96606 (2006)
[2] S. Joyce, F. Murphy-Armando and S. Fahy, *Phys. Rev. B*, **75**, 155201 (2007)
[3] F. Murphy-Armando and S. Fahy, *Phys. Rev. B*, **78**, 35202 (2008)

Carrier scattering from supercell calculations

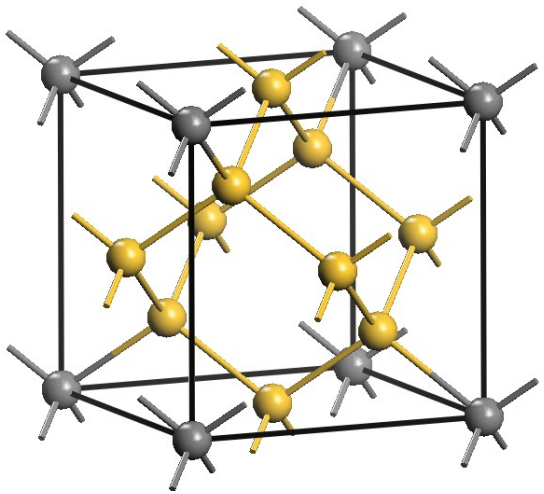
(1) Construct a supercell (SC) of pure Si



(2) Calculate ground state density and hence eigenstates / eigenvalues

Perturbation causes splitting of degenerate levels related to scattering

(3) Construct an SC with single C impurity



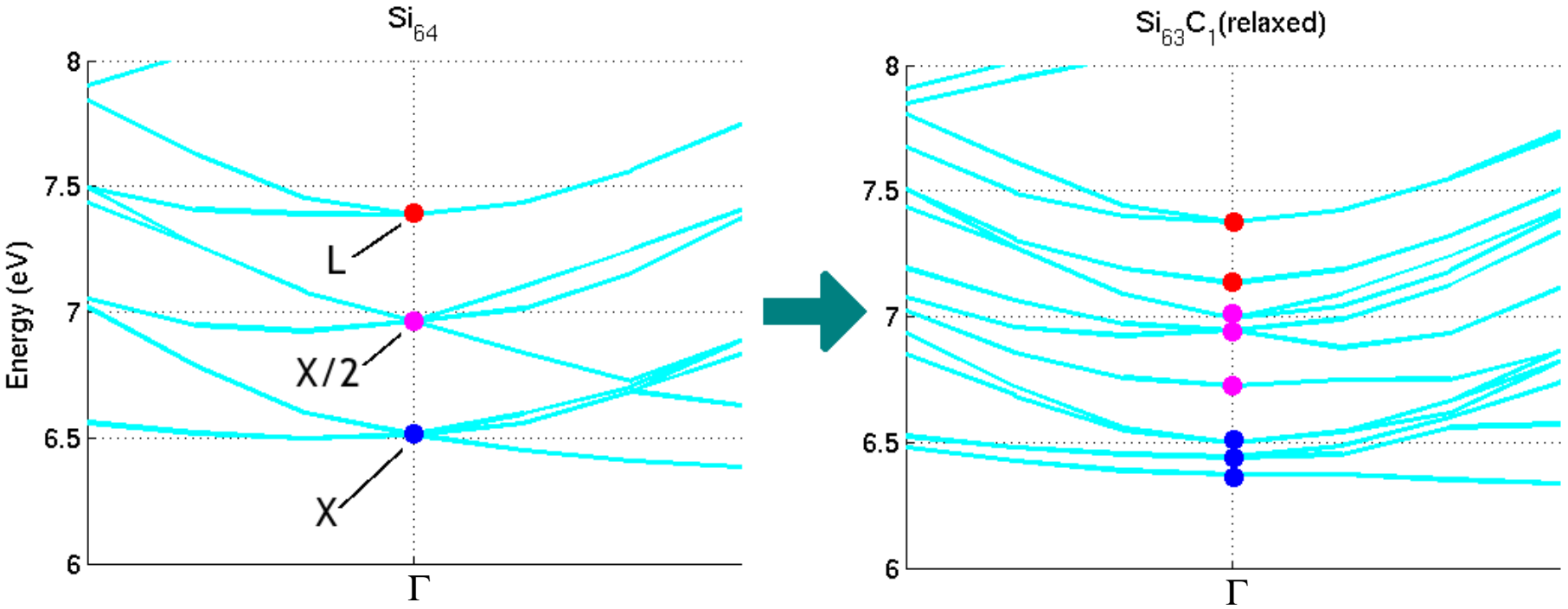
(4) Calculate new eigenstates / eigenvalues

Scattering cross-section $\propto (\Delta E)^2 D(E)$
(D(E) is density of states)

(8-atom cell used for illustration)

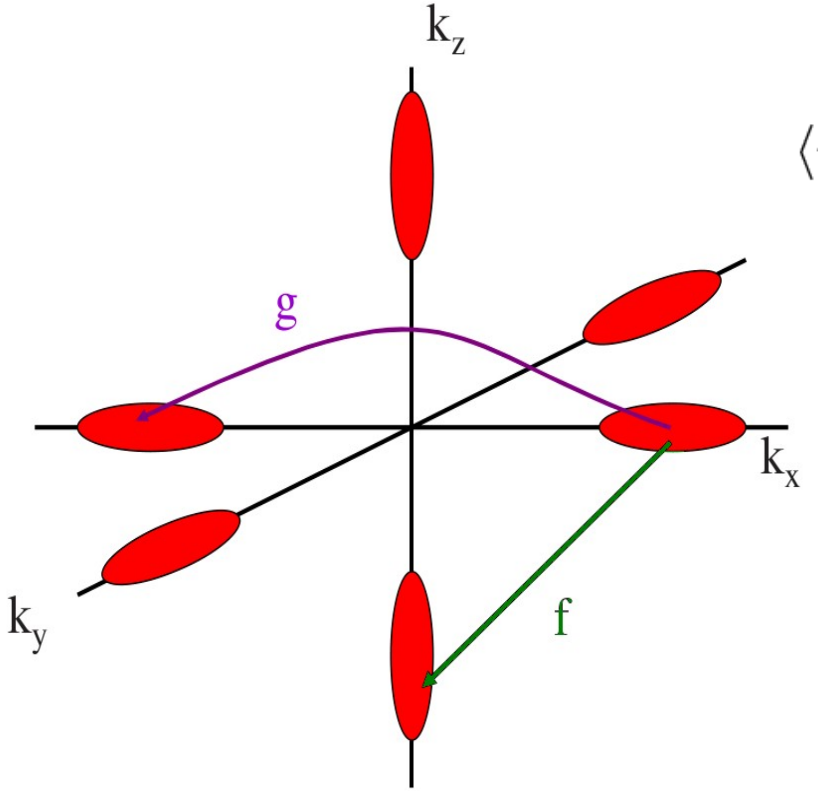
Periodic boundary conditions on supercell Brillouin zone lead to degenerate k-points being folded back onto the gamma point

Example: 64 atom supercell – single carbon atom in silicon (relaxed).



- X point: 6-fold degenerate -> non-degenerate + 2-fold + 3-fold
- Δ point: 6-fold degenerate -> non-degenerate + 2-fold + 3-fold
- L point: 4-fold degenerate -> non-degenerate + 3-fold

Intervalley and intravalley scattering on Δ line



g and *f*-type intervalley scattering
[image from *Phys. Rev. B*, **78**, 35202 (2008)]

V_Δ = intravalley, V_g = *g*-type, V_f = *f*-type

$$\langle \psi_\alpha | \, \Delta V \, | \psi_\beta \rangle = \begin{bmatrix} V_\Delta & V_g & V_f & V_f & V_f & V_f \\ V_g & V_\Delta & V_f & V_f & V_f & V_f \\ V_f & V_f & V_\Delta & V_g & V_f & V_f \\ V_f & V_f & V_g & V_\Delta & V_f & V_f \\ V_f & V_f & V_f & V_f & V_\Delta & V_g \\ V_f & V_f & V_f & V_f & V_g & V_\Delta \end{bmatrix}$$

Eigenvalues:

ΔE_1 (non-degenerate)
ΔE_2 (2-fold degenerate)
ΔE_3 (3-fold degenerate)

$$V_\Delta = \frac{1}{6}\left(\Delta E_1 + 2\Delta E_2 + 3\Delta E_3\right)$$

$$V_g = \frac{1}{6}\left(\Delta E_1 + 2\Delta E_2 - 3\Delta E_3\right)$$

$$V_f = \frac{1}{6}\left(\Delta E_1 - \Delta E_2\right)$$

The scattering matrix for first principles calculations

Perturbed eigenstate $|\phi\rangle$, unperturbed eigenstate $|\psi\rangle$

Require $|\phi\rangle \rightarrow |\psi\rangle$ far from impurity. But no eigenstate $|\phi_i\rangle$ will satisfy this, so we construct the state with the greatest overlap:

$$|\phi_\beta\rangle = \sum_{i=1}^{M} |\phi_i\rangle \langle\phi_i|\psi_\beta\rangle$$

(*M* is the number of perturbed eigenstates to sum over)

This is used in the construction of the scattering matrix:

$$\begin{aligned} \langle\psi_\alpha| \Delta V |\phi_\beta\rangle &= \langle\psi_\alpha| \Delta V \sum_{i=1}^{M} |\phi_i\rangle \langle\phi_i|\psi_\beta\rangle \\ &= \sum_{i=1}^{M} \Delta E_i^\alpha \langle\psi_\alpha|\phi_i\rangle \langle\phi_i|\psi_\beta\rangle , \end{aligned}$$

$$\text{where } \Delta E_i^\alpha = E_i - E_\alpha$$

Construction of $\langle \psi_\alpha | \, \Delta V \, | \phi_\beta \rangle$

$$\begin{bmatrix} V_{11} & V_{12} & V_{13} & V_{14} & V_{15} & V_{16} & \cdots & & & \cdots & V_{1n} \\ V_{21} & V_{22} & V_{23} & V_{24} & V_{25} & V_{26} & \cdots & & & \cdots & V_{2n} \\ V_{31} & V_{32} & V_{33} & V_{34} & V_{35} & V_{36} & \cdots & & & & \vdots \\ V_{41} & V_{42} & V_{43} & V_{44} & V_{45} & V_{46} & \cdots & & & & \\ V_{51} & V_{52} & V_{53} & V_{54} & V_{55} & V_{56} & \cdots & & & & \\ V_{61} & V_{62} & V_{63} & V_{64} & V_{65} & V_{66} & \cdots & & & & \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & & V_{77} & V_{78} & V_{79} & V_{7,10} & V_{7,11} & V_{7,12} \\ & & & & & & & V_{87} & V_{88} & V_{89} & V_{8,10} & V_{8,11} & V_{8,12} \\ & & & & & & & V_{97} & V_{98} & V_{99} & V_{9,10} & V_{9,11} & V_{9,12} \\ & & & & & & & V_{10,7} & V_{10,8} & V_{10,9} & V_{10,10} & V_{10,11} & V_{10,12} \\ & & & & & & & V_{11,7} & V_{11,8} & V_{11,9} & V_{11,10} & V_{11,11} & V_{11,12} \\ & & & & & & & V_{12,7} & V_{12,8} & V_{12,9} & V_{12,10} & V_{12,11} & V_{12,12} \\ \vdots & \vdots & & & & & & & & & & \ddots & \vdots \\ V_{n1} & V_{n2} & \cdots & & & & & & & & & \cdots & V_{nn} \end{bmatrix}$$

Extract sub-matrices corresponding to originally degenerate states...

$$\begin{bmatrix} V_\Delta & V_g & V_f & V_f & V_f & V_f \\ V_g & V_\Delta & V_f & V_f & V_f & V_f \\ V_f & V_f & V_\Delta & V_g & V_f & V_f \\ V_f & V_f & V_g & V_\Delta & V_f & V_f \\ V_f & V_f & V_f & V_f & V_\Delta & V_g \\ V_f & V_f & V_f & V_f & V_g & V_\Delta \end{bmatrix}$$

... and diagonalise to find eigenvalues and scattering parameters.

Carbon in silicon - motivation

- Strain compensation in SiGe/Si heterostructures
- Suppression of dopant diffusion during growth

What effect will substitutional carbon have on the mobility?

- Require knowledge of carrier scattering

Effect of carbon doping on carrier mobility

n-type mobility

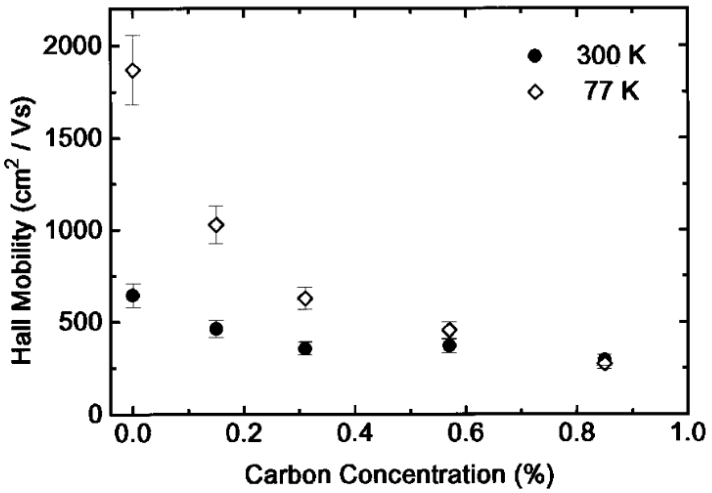


FIG. 3. Experimentally obtained electron mobilities at 300 and 77 K as a function of carbon content in homogeneously Sb-doped $Si_{1-y}C_y$ layers on Si(001).

p-type mobility

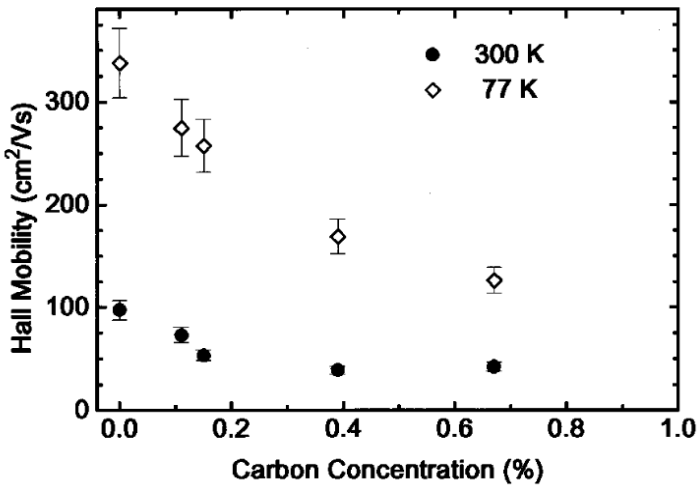


FIG. 6. Experimentally obtained hole mobilities at 300 and 77 K as a function of carbon content in homogeneously B-doped $Si_{1-x-y}Ge_xC_y$ layers on Si(001).

H.J. Osten and P. Gaworzewski, *J. Appl. Phys.*, **82**, 4977 (1997)

Density functional calculations

- Self consistent field (SCF) calculations for the ground state density
  - Pseudopotentials
    - Troullier-Martins [1]
  - Construction of supercells
  - Choice of k-grid
    - Shifted Monkhorst-Pack grid [2]
    - Use k-grid analysis option in ABINIT
  - Cut-off energy
    - 40 Hartree (based on convergence of 8-atom supercell)
  - Ionic relaxation algorithm
    - Modified Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization [3-4]
- Calculations for band structure using ground state density

[1] N. Troullier and J.L. Martins. Efficient pseudopotentials for plane-wave calculations. Physical Review B, **43**, 1993, 1991.

[2] H.J. Monkhorst and J.D. Pack. Special points for Brillouin-zone integrations. *Physical Review B*, **13**, 5188, 1976.

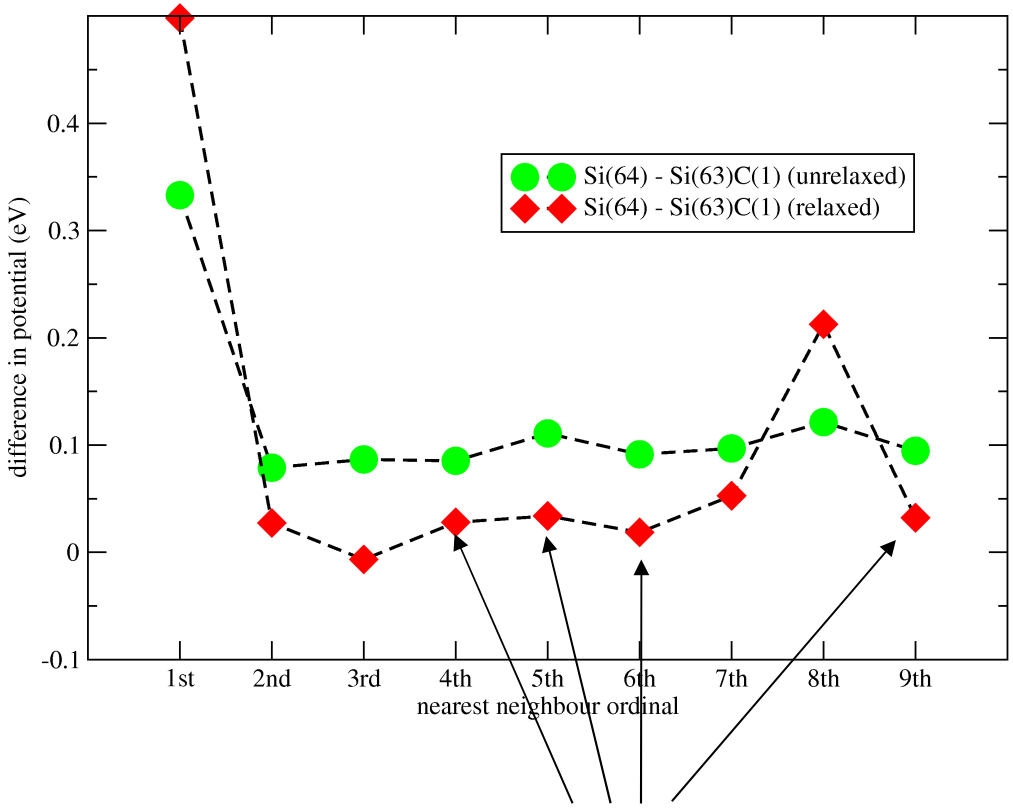
[3] CG Broyden. Quasi-Newton methods and their application to function minimisation. *Mathematics of Computation*, **21,** 368, 1967; CG Broyden. The convergence of a class of double-rank minimization algorithms 1. general considerations. IMA Journal of *Applied Mathematics*, **6**, 76, 1970; R. Fletcher. A new approach to variable metric algorithms. *The Computer Journal*, **13**, 317, 1970; D. Goldfarb. A family of variable-metric methods derived by variational means. *Mathematics of Computation*, **24**, 23, 1970; DF Shanno. Conditioning of quasi-Newton methods for function minimization. *Mathematics of Computation*, 647, 1970.

[4] H.B. Schlegel. Optimization of equilibrium geometries and transition structures. *Journal of Computational Chemistry*, **3**, 214, 1982.

The potential energy reference

(64 atom supercell)

Difference in total potential at atomic positions



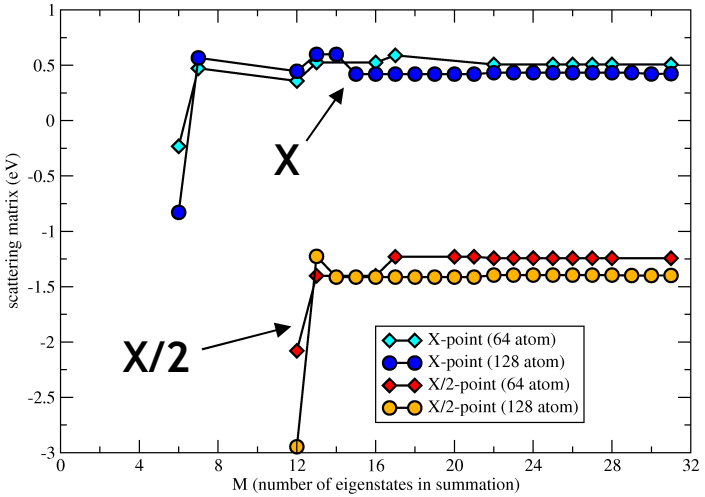
We require the absolute shifts in energy to calculate intravalley scattering

Differences found at atomic positions.

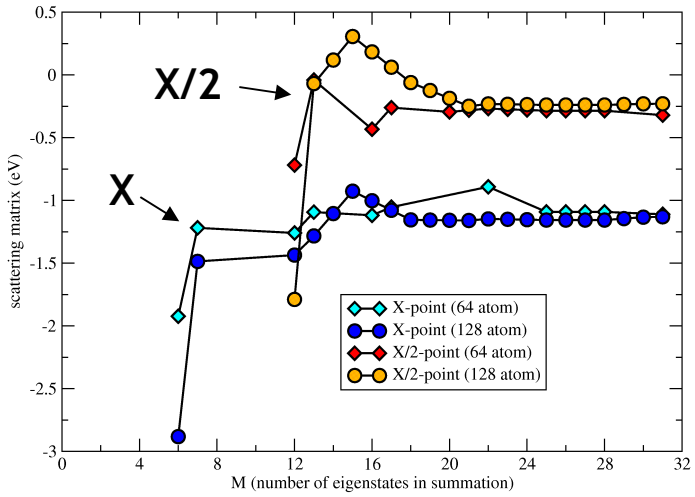
These points averaged and standard deviation calculated (for estimation of error)

Scattering parameters

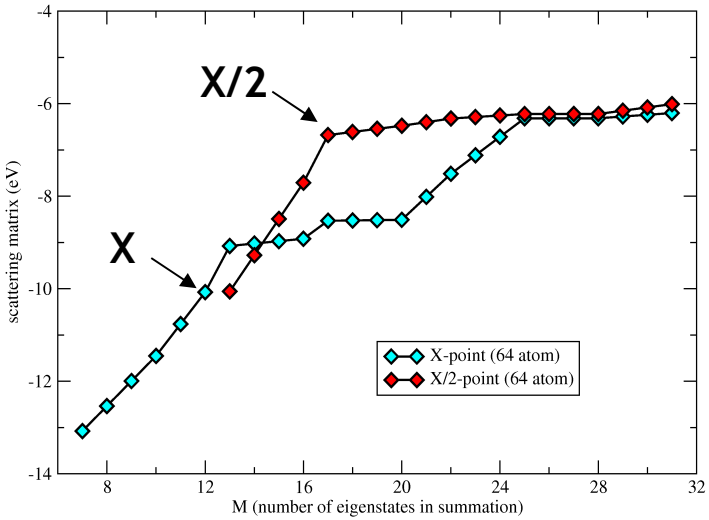
f-type intervalley scattering



g-type intervalley scattering



intravalley scattering



Reminder:

$$|\phi_\beta\rangle = \sum_{i=1}^{M} |\phi_i\rangle \langle\phi_i|\psi_\beta\rangle$$

Scattering parameters multiplied by cell size

Plotted against M (number of eigenstates in expansion)

M=28 (number of eigenstates used in summation)

values in eV

	X	X/2	Δ min
intra	-6.3	-6.2	-6.3 ±2.6
f-type	0.51	-1.24	0.03
g-type	-1.09	-0.29	-0.84

(scattering at Δ minimum found via interpolation)

Conclusions

- Intravalley scattering ~6 eV (cross-section $\propto |\Delta E|^2$)
  - Order of magnitude greater than g-type scattering
  - About 50% that of nitrogen in GaAs
  - Order of magnitude greater than intravalley alloy scattering in SiGe
- g-type scattering an order of magnitude greater than f-type at Δ minimum
  - However, at X and X/2 points, scattering matrices are comparable (the interpolation of f-type scattering at the Δ minimum requires crossing zero)
  - g-type scattering comparable to intervalley alloy scattering in SiGe
- Outstanding issues:
  - Mobility calculations will need to incorporate phonon scattering and the effect of strain (in real structures of interest)
  - However, quantitatively, large possible error (40%) in intravalley scattering due to uncertainty in common potential reference
  - More complete investigation of supercell size dependence

Acknowledgements

The authors would like to thank Philip Murphy-Armando for many very useful discussions.

This work is support by the Science Foundation Ireland.