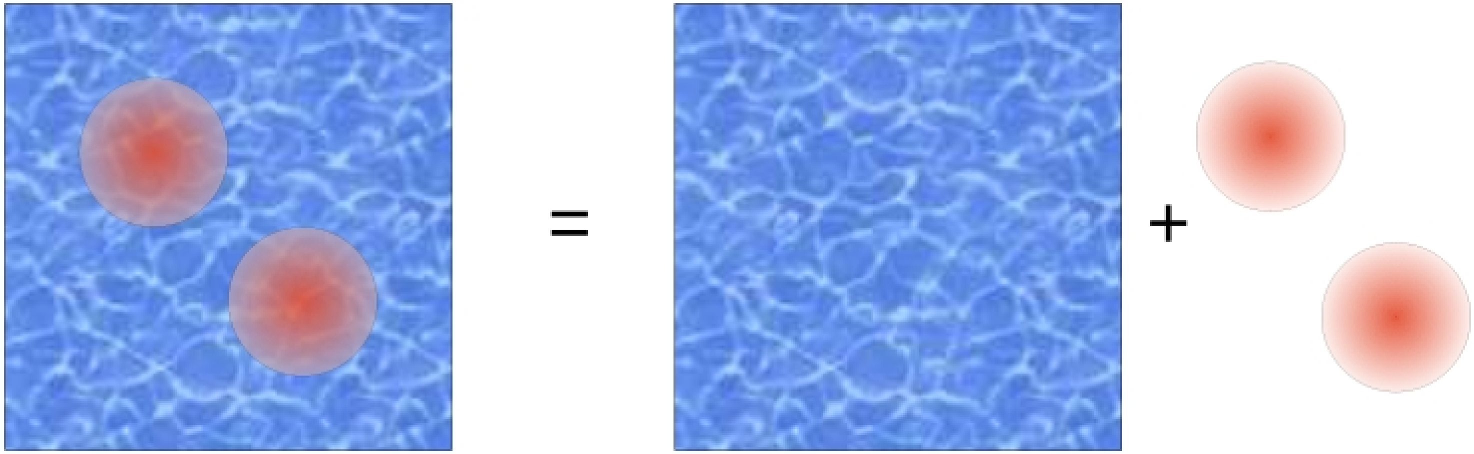
# Summary of PAW calculation method

Given the PAW transformation for a valence wavefunction:

$$\Psi_v(\mathbf{r}) = \widetilde{\Psi}_v(\mathbf{r}) + \sum_{ai} \left( \phi_i^a(\mathbf{r} - \mathbf{R}^a) - \widetilde{\phi}_i^a(\mathbf{r} - \mathbf{R}^a) \right) \langle p_i^a | \widetilde{\psi}_v \rangle,$$

it is also possible to evaluate the valence electron energy of the system in the form:

$$E_{tot}^{\text{vale}} = \underbrace{\widetilde{E}_{tot}}_{\text{pseudo energy}} + \sum_a \underbrace{\left( E_{tot}^a - \widetilde{E}_{tot}^a \right)}_{\text{atom-centered corrections}} .$$



The smooth contributions are given by

$$\begin{aligned}\tilde{E} = \quad & \tilde{K} + \frac{e^2}{2} \int d^3r \int d^3r' \frac{(\tilde{n}(\mathbf{r}) + \tilde{n}_{\text{core}}(\mathbf{r}) + \hat{n}(\mathbf{r}))(\tilde{n}(\mathbf{r}') + \tilde{n}_{\text{core}}(\mathbf{r}') + \hat{n}(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} \\ & + \int d^3r\, \tilde{v}_{\text{loc}}(\mathbf{r})\tilde{n}(\mathbf{r}) + E_{xc}[\tilde{n}_{\text{core}} + \tilde{n}].\end{aligned}$$

For the Bloch wavefunction $\Psi_{n\mathbf{k}}(\mathbf{r})$, with an occupancy of $o_{n\mathbf{k}}$, the smooth density is given by

The one-center terms are given by

$$\begin{aligned}E^a - \tilde{E}^a = & \sum_{ij} W^a_{ij} \left( K^a_{ij} + [v^a_{\text{at}}]_{ij} - [\hat{v}^a]_{ij} + \frac{1}{2}[V^a_{\text{H}}]_{ij} \right) \\ & + (E_{\text{xc}}[n^a_{\text{core}} + n^a] - E_{\text{xc}}[\tilde{n}^a_{\text{core}} + \tilde{n}^a]) - \hat{E}^a - \tilde{E}^a_{\text{core}} - Q_{00}\tilde{E}^a_{\text{core-hat}}.\end{aligned}$$

Here,

$$W^a_{ij} \equiv \sum_{n\mathbf{k}} o_{n\mathbf{k}} \langle \Psi_{n\mathbf{k}} | p^a_i \rangle \langle p^a_j | \Psi_{n\mathbf{k}} \rangle.$$

# 3 PAW Hamiltonian

In terms of these basis functions, the generalized eigenvalue equation for the PAW formalism can be written

$$\mathbf{H}^{\mathbf{PAW}}(\mathbf{r})|\tilde{\Psi}_E(\mathbf{r})\rangle = E\mathbf{O}|\tilde{\Psi}_E(\mathbf{r})\rangle, \tag{36}$$

$$\mathbf{H}^{\mathbf{PAW}} \equiv \tilde{H}(\mathbf{r}) + \sum_{aij} |\tilde{p}_i^a\rangle \left(\langle\phi_i^a|H^a|\phi_j^a\rangle - \langle\tilde{\phi}_i^a|\tilde{H}^a|\tilde{\phi}_j^a\rangle\right) \langle\tilde{p}_j^a| \equiv \tilde{H}(\mathbf{r}) + \sum_{aij} |\tilde{p}_i^a\rangle D_{ij}^a \langle\tilde{p}_j^a|.$$

The overlap term is given by

$$\mathbf{O} \equiv \mathbf{1} + \sum_{aij} |\tilde{p}_i^a\rangle \left(\langle\phi_i^a|\phi_j^a\rangle - \langle\tilde{\phi}_i^a|\tilde{\phi}_j^a\rangle\right) \langle\tilde{p}_j^a|.$$

# Calculating forces on atoms at fixed unit cell volume

The force on an atom $a$ at the site $\mathbf{R}^a$ is given by

$$\mathbf{F}^a \equiv -\left\{\nabla_{\mathbf{R}^a}\left[E\right]\right\} = \frac{4\pi i e^2}{\mathcal{V}} \sum_{\mathbf{G}\neq\mathbf{0}} \frac{\mathbf{G}\;\left[\bar{\hat{n}}^a(\mathbf{G}) + \bar{\tilde{n}}^a_{\text{core}}(\mathbf{G})\right]\left[\bar{\tilde{n}}^*(\mathbf{G}) + \bar{\hat{n}}^*(\mathbf{G}) + \bar{\tilde{n}}^*_{\text{core}}(\mathbf{G})\right]}{G^2}$$

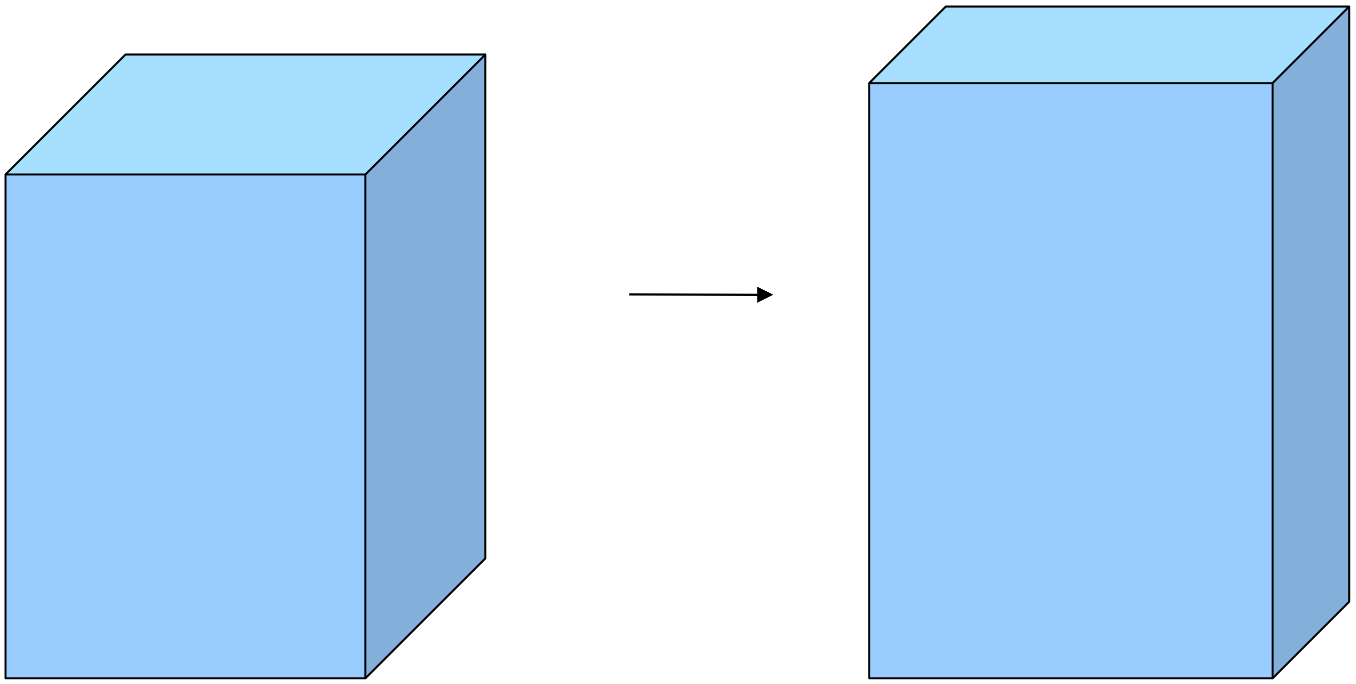
$$+\frac{i}{\mathcal{V}} \sum_{\mathbf{G}\neq\mathbf{0}} \mathbf{G}\; \bar{\tilde{v}}^a_{\text{loc}}(\mathbf{G})\bar{\tilde{n}}*(\mathbf{G}) + \frac{i}{\mathcal{V}} \sum_{\mathbf{G}\neq\mathbf{0}} \mathbf{G}\; \bar{\tilde{n}}^a_{\text{core}}(\mathbf{G})\bar{V}^*_{\text{xc}}(\mathbf{G}) - \sum_{ij}\left\{\nabla_{\mathbf{R}^a}\left[W^a_{ij}\right]\right\} D^a_{ij} + \sum_{ij}\left\{\nabla_{\mathbf{R}^a}\left[U^a_{ij}\right]\right\} O^a_{ij}. \tag{73}$$

The first contribution depends on the Fourier transform of the atom-centered compensation and coretail charges and the second contribution depends on the Fourier transform of the atom centered local potential (Eq. [3]-14). The third term represents the effects of the coretail densities in the exchange-correlation interaction. The last term of the force equation involves a weighted projected occupation coefficient which we define according to

$$U^a_{ij} \equiv \sum_{n\mathbf{k}} o_{n\mathbf{k}} E_{n\mathbf{k}} \langle \tilde{\Psi}_{n\mathbf{k}} | \tilde{p}^a_i \rangle \langle \tilde{p}^a_j | \tilde{\Psi}_{n\mathbf{k}} \rangle. \tag{74}$$

The gradient with respect to the atomic position of both $W^a_{ij}$ and $U^a_{ij}$ depends on the gradient of the matrix elements $\langle \nabla_{\mathbf{R}^a}[\tilde{p}^a_i] | \tilde{\Psi}_{n\mathbf{k}} \rangle$ which can be conveniently evaluated in Fourier space using

# Optimization of the full crystal structure including variation in unit cell



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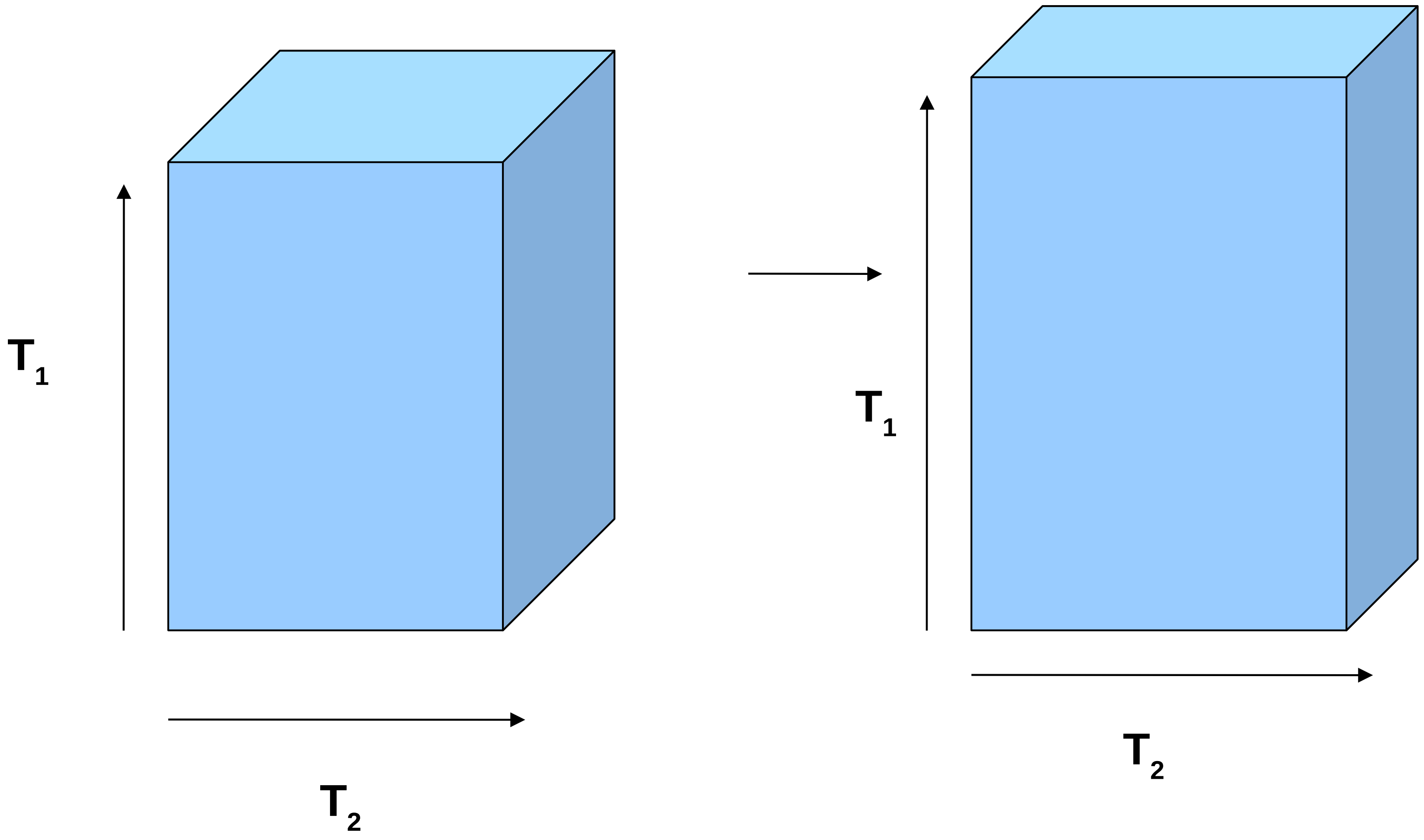

# Example of structural optimization studies

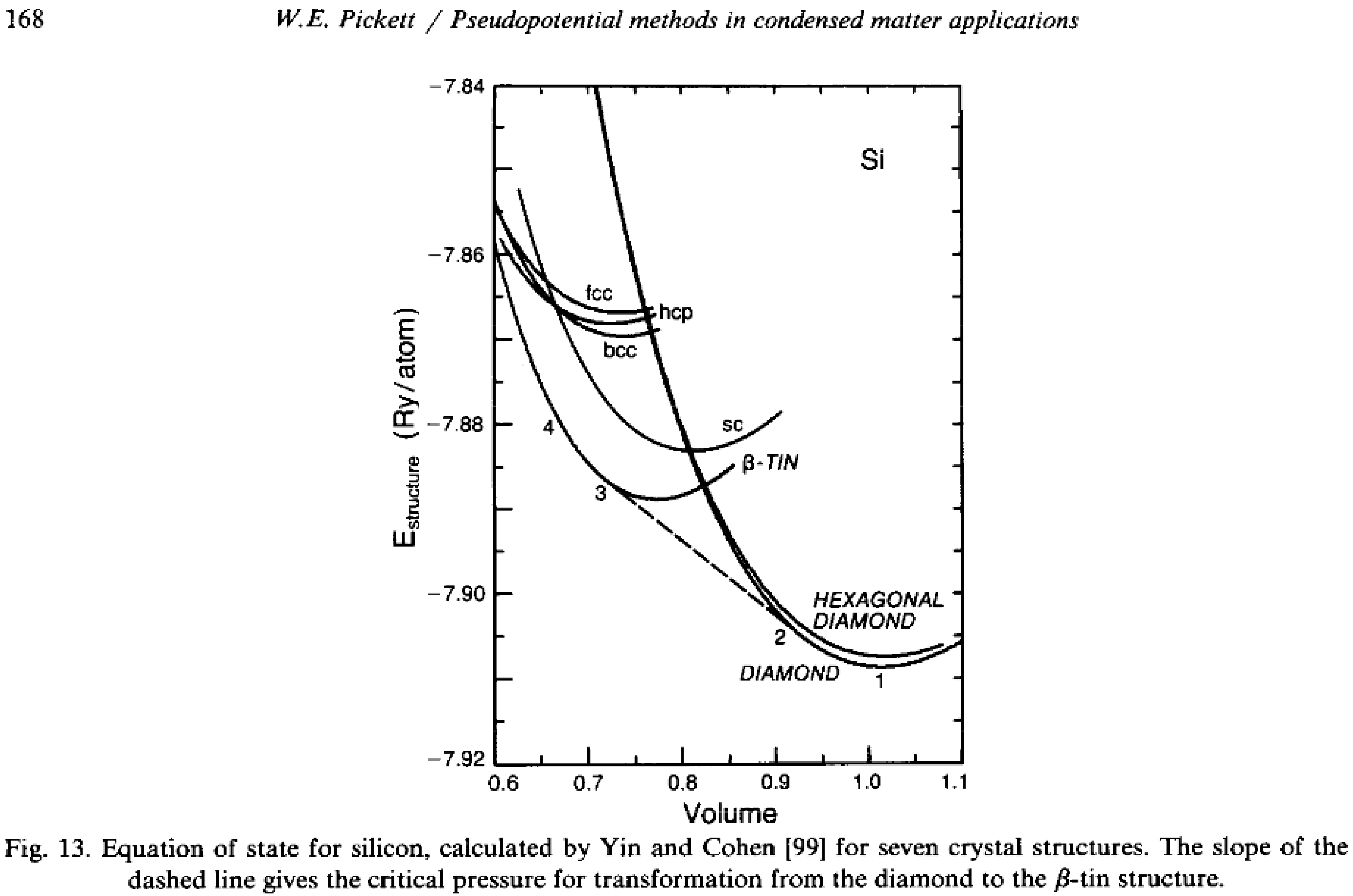

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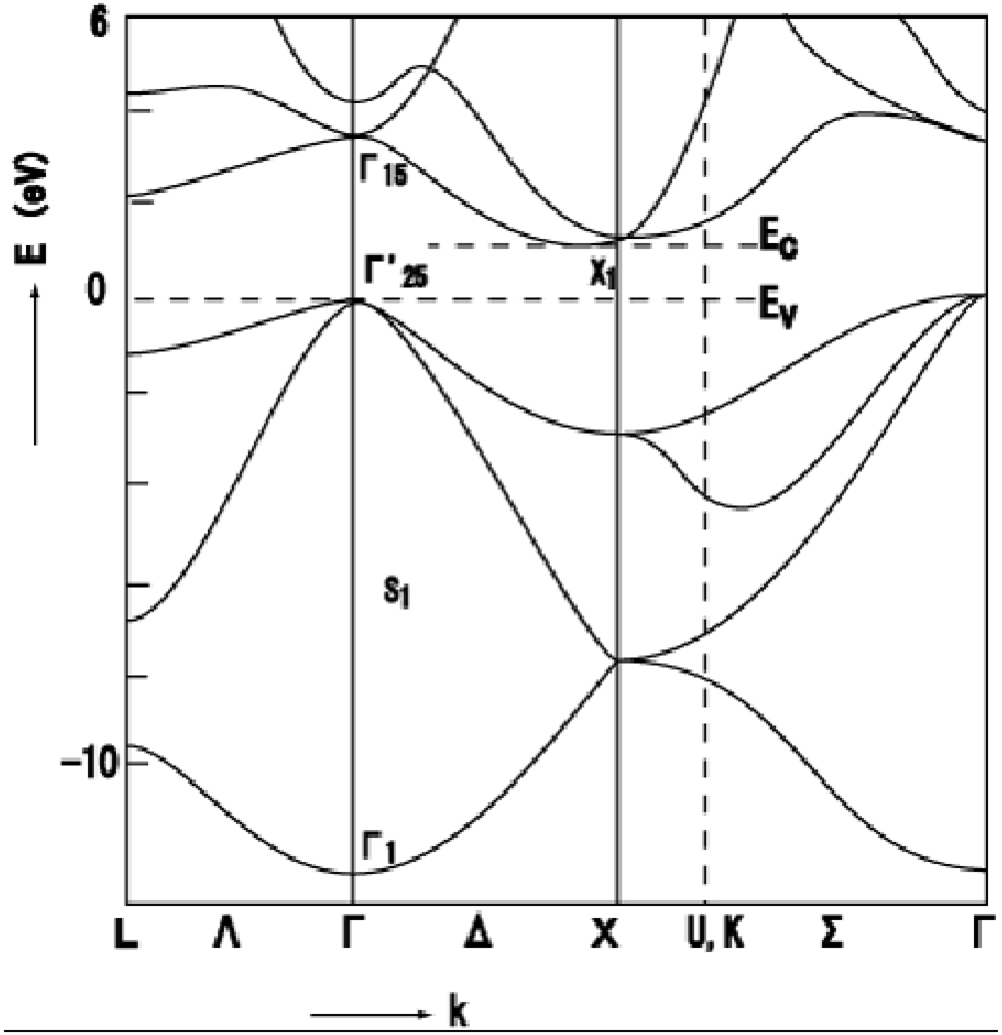
Fig. 13. Equation of state for silicon, calculated by Yin and Cohen [99] for seven crystal structures. The slope of the dashed line gives the critical pressure for transformation from the diamond to the $\beta$-tin structure.

Yin and Cohen, PRB 26 5668 (1982)

# Electronic structure of Si



# Calculation of optical properties

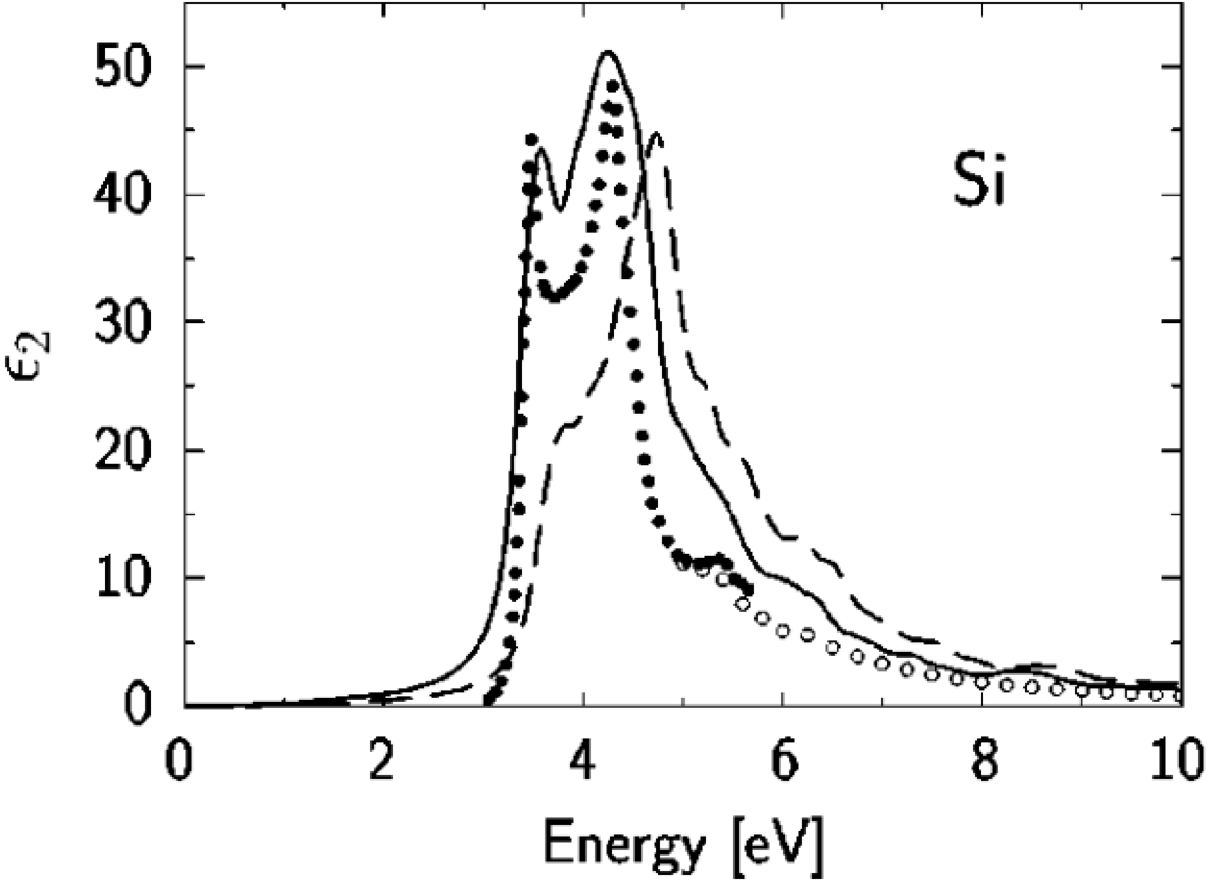


FIG. 8. Calculated optical absorption spectrum of Si with (solid lines) and without (dashed lines) electron-hole interaction, using three valence bands, six conduction bands, 500 **k** points in the BZ, and an artificial broadening of 0.15 eV. Experimental data are taken from Ref. 34 (○) and Ref. 35 (●).

From: M. Rohfling and S. G. Louie, PRB 62 4927-4944 (2000)