Precise effective masses from Density Functional Perturbation Theory

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J. Laflamme-Janssen et al, Phys. Rev. B93, 205147 (2016)

Motivation

Effective mass = key concept in understanding

Mobility, thermoelectric properties, magnetic response …

Example : search for Transparent Conducting Oxides (TCOs)

(for transparent electronics)

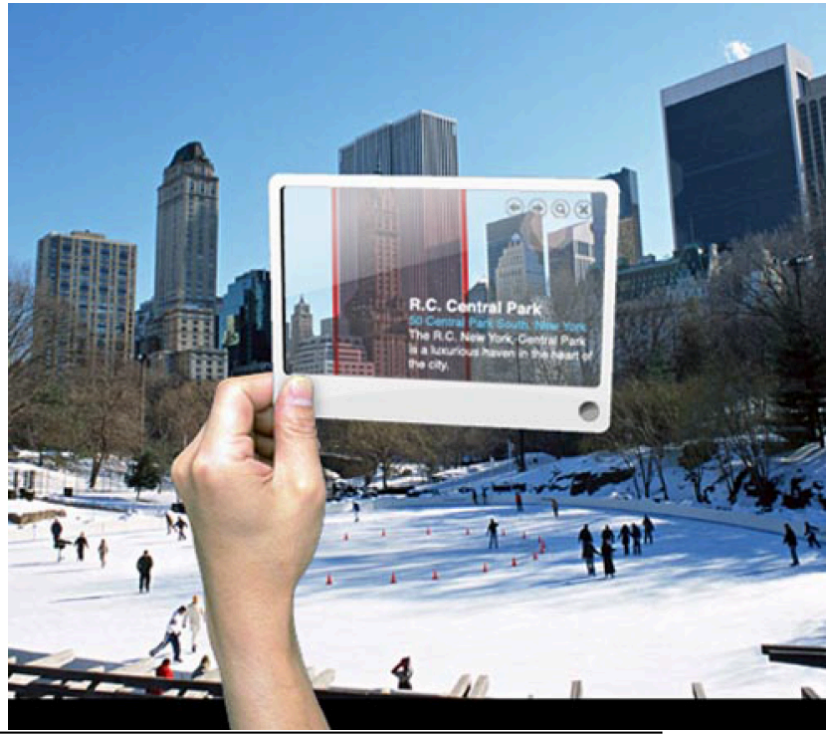
n-type TCOs ubiquitous in current technologies

by contrast, p-type TCOs are lagging behind

- best n-type mobilities 100 $cm^2/(V.s)$
- best p-type mobilities 10 $cm^2/(V.s)$

Mobility directly linked to effective mass

$$\mu = \frac{e\tau}{m^*}$$



What is an effective mass ?

"Inertia" when reacting to force. F=ma.

In quantum mechanics + periodic system :

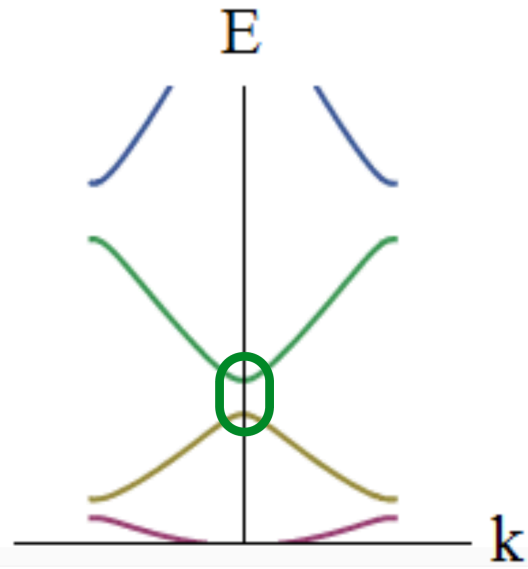
Force = “r” operator => d/dk

Velocity = group velocity = dε/dk

$$\varepsilon_{kn} \approx \varepsilon_{\Gamma n} + \frac{k^2}{2M}$$

$$\varepsilon_{\underline{k}n} \approx \varepsilon_{\Gamma n} + \tfrac{1}{2}\underline{k}^T \underline{\underline{M}}^{-1}_{\Gamma n} \underline{k}$$

$$\left(\underline{\underline{M}}^{-1}_{n}\right)^{\alpha\beta} = \frac{\partial^2 \varepsilon_n}{\partial \underline{k}_\alpha \partial \underline{k}_\beta} \equiv \varepsilon_n^{\alpha\beta}$$

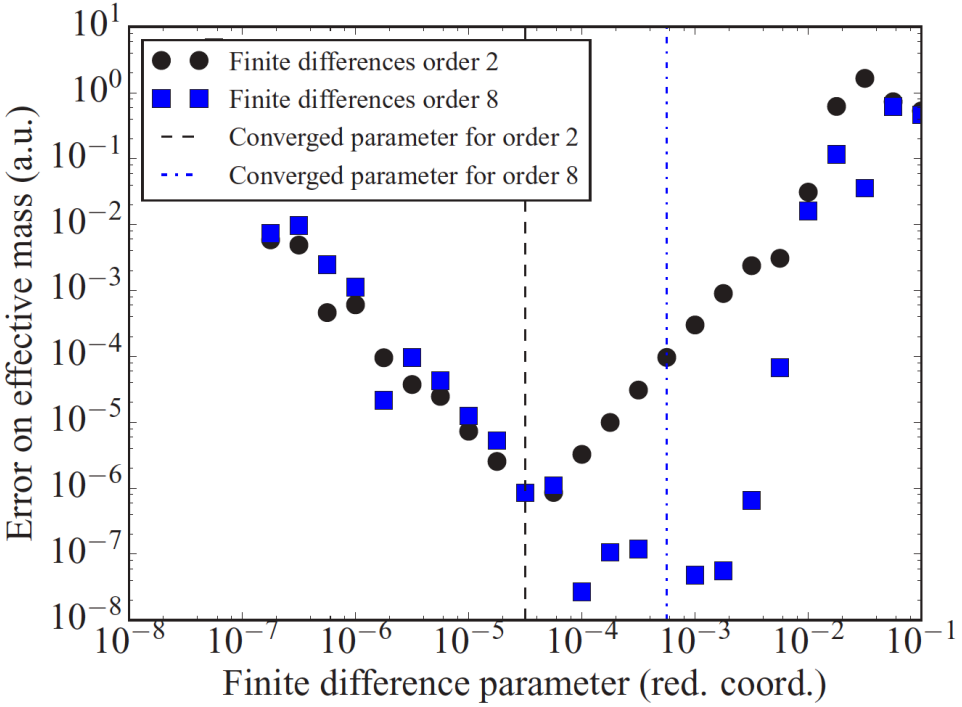


How to compute effective mass tensor ?

$$\left(\underline{\underline{M}}_n^{-1}\right)^{\alpha\beta} = \frac{\partial^2 \varepsilon_n}{\partial \underline{k}_\alpha \, \partial \underline{k}_\beta} \equiv \varepsilon_n^{\alpha\beta}$$

Finite difference ?

“Usual” procedure …



But precision ?

Tensor characteristics when insufficient symmetry ?

Degeneracy ?

DFPT approach

$$\left(\underline{\underline{M}}_n^{-1}\right)^{\alpha\beta} = \frac{\partial^2 \varepsilon_n}{\partial \underline{k}_\alpha \partial \underline{k}_\beta} \equiv \varepsilon_n^{\alpha\beta} \qquad \alpha\beta = \{xx, yy, zz, xy, yz, xz\}$$

$$= \langle \psi_n | \hat{H} | \psi_n \rangle^{\alpha\beta}$$

$$= \langle \psi_n | \hat{H}^{\alpha\beta} | \psi_n \rangle$$

$$+ \left(\langle \psi_n^{\alpha} | \hat{H}^{\beta} | \psi_n \rangle + \alpha \leftrightarrow \beta \right) + cc.$$

$$+ \langle \psi_n^{\alpha} | \hat{H} - \varepsilon_n | \psi_n^{\beta} \rangle + cc.$$

First-order wavefunctions : Sternheimer equation…

$$\left(\hat{H} - \varepsilon_n\right) | \psi_n^{\alpha} \rangle = \left(\hat{H}^{\alpha} - \varepsilon_n^{\alpha}\right) | \psi_n \rangle$$

1st and 2nd-order matrix elements

$$\langle \underline{G}|\hat{H}_{\underline{k}}|\underline{G}'\rangle = \frac{(\underline{k}+\underline{G})^2}{2}\delta_{\underline{G}\underline{G}'} + V_{\underline{G}-\underline{G}'} + \tilde{V}_{\underline{k},\underline{G}\underline{G}'}$$

DFT potential: $\langle \underline{r}|\hat{V}|\underline{r}'\rangle = V(\underline{r})\delta(\underline{r}-\underline{r}')$

Pseudopotential: $\langle \underline{r}|\hat{\tilde{V}}|\underline{r}'\rangle = \tilde{V}(\underline{r},\underline{r}')$

$$\langle \underline{G}|\hat{H}^{\alpha}_{\underline{k}}|\underline{G}'\rangle = (\underline{k}+\underline{G})_{\alpha}\,\delta_{\underline{G}\underline{G}'} + 0 + \tilde{V}^{\alpha}_{\underline{k},\underline{G}\underline{G}'}$$

$$\langle \underline{G}|\hat{H}^{\alpha\beta}_{\underline{k}}|\underline{G}'\rangle = \delta_{\alpha\beta}\delta_{\underline{G}\underline{G}'} + 0 + \tilde{V}^{\alpha\beta}_{\underline{k},\underline{G}\underline{G}'}$$

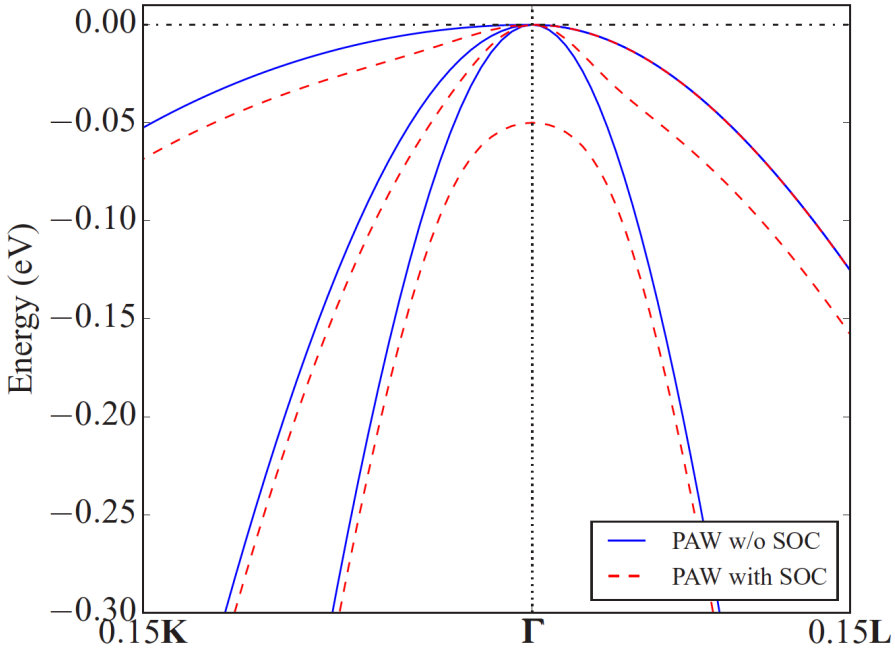
$$\langle \underline{G}|\hat{\tilde{V}}_{\underline{k}}|\underline{G}'\rangle = \sum_{ij}\langle \underline{k}+\underline{G}|p_i\rangle D_{ij}\langle p_j|\underline{k}+\underline{G}'\rangle$$

$$\langle \underline{k}+\underline{G}|p_i\rangle \propto e^{i(\underline{k}+\underline{G})\cdot\underline{r}} Y_{l_i m_i}\left(\frac{\underline{k}+\underline{G}}{|\underline{k}+\underline{G}|}\right)\int_0^{r_c} dr\, p_i(r)\, j_{l_i}(|\underline{k}+\underline{G}|r)$$

Degeneracy

For example, 3-fold degeneracy of top of valence band of silicon…

$$\left(\underline{\underline{M}}_n^{-1}\right)^{\alpha\beta} = \frac{\partial^2 \varepsilon_n}{\partial \underline{k}_\alpha \partial \underline{k}_\beta} \equiv \varepsilon_n^{\alpha\beta} \qquad ?$$



Normally, one would try to diagonalize this quantity in degenerate subspace.

But there are 6 such tensors, that cannot be diagonalized simultaneously !

Solution (Luttinger & Kohn, Phys. Rev. 97, 869 (1955))

Compute a matrix of tensors !

$$\left\langle n \middle| \hat{H}^{\alpha\beta} \middle| n' \right\rangle \neq 0$$

Then, the direction dependence is NOT tensorial.

$$\varepsilon_{nn'}(\underline{k}) \approx \frac{1}{2} \underline{k}^T \underline{\underline{M}}_{nn'}^{-1} \underline{k} = \frac{k^2}{2} \hat{k}(\theta,\phi)^T \underline{\underline{M}}_{nn'}^{-1} \hat{k}(\theta,\phi) = \frac{k^2}{2} M_{nn'}^{-1}(\theta,\phi)$$

For details see : J. Laflamme-Janssen et al, Phys. Rev. B93, 205147 (2016)

Tests

Direction	(100)	(111)	(110)
Band 2			
FD order 8	–0.167 180 44	–0.093 807 82	–0.105 369 00
DFPT	–0.167 180 40	–0.093 807 80	–0.105 368 95
DFPT-FD 8	–4E-8	–3E-8	–5E-8
Band 3			
FD order 8	–0.257 803 79	–0.649 497 22	–0.257 803 80
DFPT	–0.257 803 82	–0.649 497 35	–0.257 803 82
DFPT-FD 8	3E-8	1E-7	2E-8
Band 4			
FD order 8	–0.257 803 82	–0.649 497 16	–2.702 563 30
DFPT	–0.257 803 82	–0.649 497 35	–2.702 563 84
DFPT-FD 8	4E-9	2E-7	5E-7

Implementation characteristics

- Norm-conserving / PAW
- Spin-polarized
- Spin-orbit (only in PAW)

As usual : DFPT outperforms completely finite-differences in convenience & precision

- ABINIT v8.0
- Test case : v7#80, 81, 82
- Input variables : efmas_XXX

Tests / examples : silicon, graphane, antimony, all with and without spin-orbit coupling, see
J. Laflamme-Janssen et al, Phys. Rev. B93, 205147 (2016)