Benchmarking exchange-correlation potentials with the mstar60 dataset

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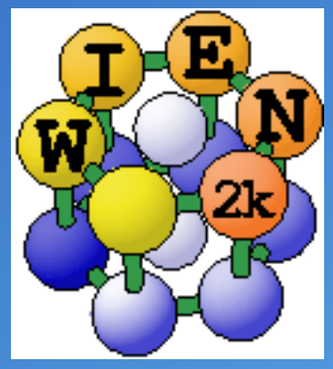
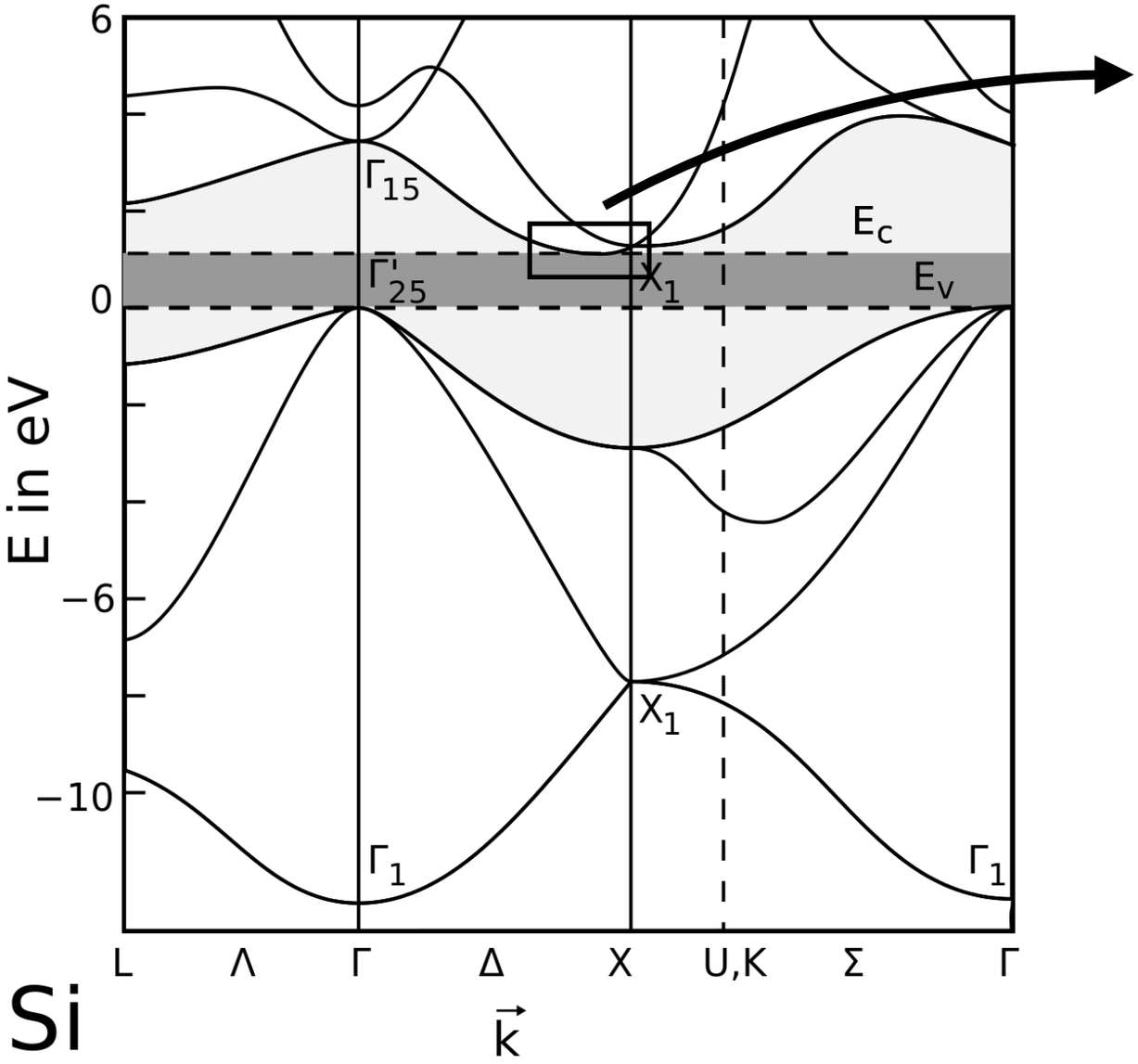
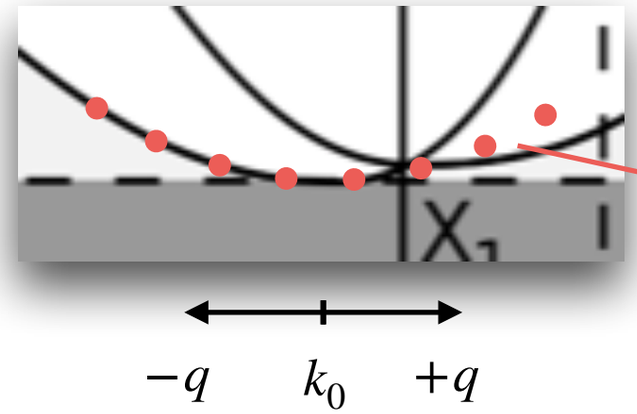


McMaster University

Effective mass





$$E(\mathbf{k}_0 + \mathbf{q}) \approx E_0(\mathbf{k}_0) + \frac{\hbar^2 \mathbf{q}^2}{2m^*}$$

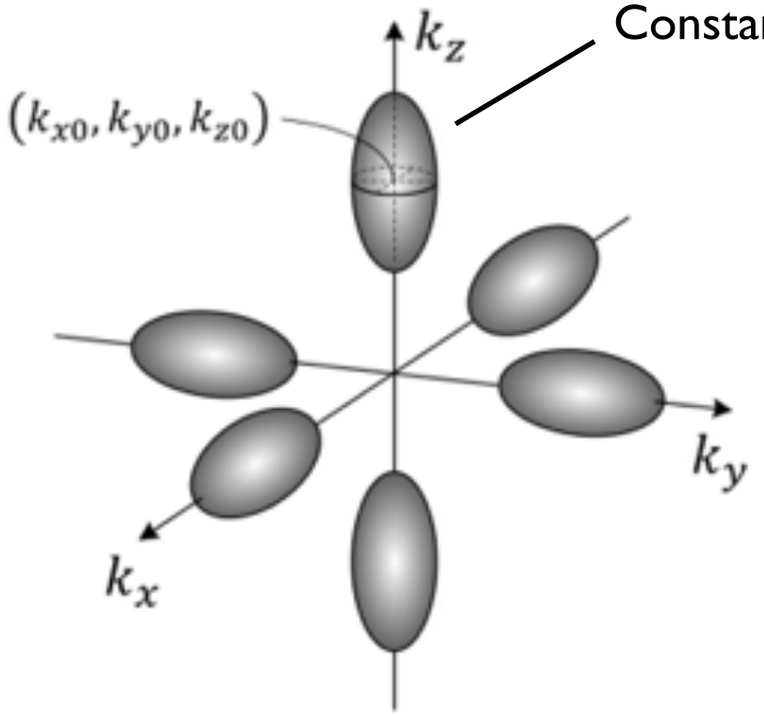
$$m^* = \hbar^2 \left(\frac{\partial^2 E}{\partial k^2} \right)^{-1}$$

Typically Si (conduction band, along <100>): $m^* \sim 0.9 m_0$
GaAs (conduction band): $m^* \sim 0.07 m_0$

Mobility of charge carriers (Drude model):

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

Effective mass as a tensor



Constant energy surface

$$E(\mathbf{k}_0 + \mathbf{q}) \approx E_0(\mathbf{k}_0) + \frac{\hbar^2}{4} \sum_{\alpha,\beta} \frac{q_\alpha q_\beta}{m^*_{\alpha\beta}} \qquad \alpha, \beta = x, y, z \text{ (or 1, 2, 3)}$$

$$m^*_{\alpha\beta} = \hbar^2 \left(\frac{\partial^2 E}{\partial k_\alpha \, \partial k_\beta} \right)^{-1}$$

need to fit "many" parabolas in 3D k-space

For Si (conduction band): $m^* \sim \begin{pmatrix} 0.9 & 0 & 0 \\ 0 & 0.2 & 0 \\ 0 & 0 & 0.2 \end{pmatrix} m_0$

generally not zero

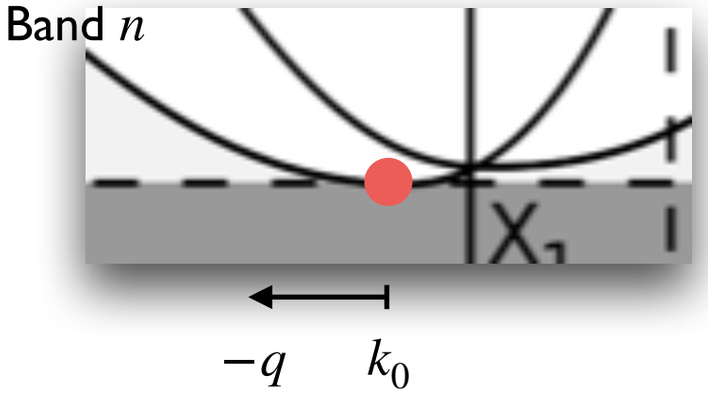
For GaAs (conduction band): $m^* \sim \begin{pmatrix} 0.07 & 0 & 0 \\ 0 & 0.07 & 0 \\ 0 & 0 & 0.07 \end{pmatrix} m_0$

"Average" conductivity mass: $$m^*_{\text{cond}} = \left[\frac{(m^*_{xx})^{-1} + (m^*_{yy})^{-1} + (m^*_{zz})^{-1}}{3} \right]^{-1}$$

Good news: $(m^*_{xx})^{-1} + (m^*_{yy})^{-1} + (m^*_{zz})^{-1}$ is <u>invariant</u> to transformation of coordinates

Challenge: Get m* <u>without</u> calculating $E(\mathbf{k})$ in the vicinity of $\mathbf{k}_0$

Perturbation theory



Unperturbed Schrödinger equation: $\hat{H}(k_0)\,|\psi_{n,k_0}\rangle = E_n(k_0)\,|\psi_{n,k_0}\rangle$

Bloch function: $\psi_{n,k_0}(x) = u_{n,k_0}(x)\,e^{ik_0x}$

Momentum matrix elements: $p_{nl,k_0} = \langle u_{n,k_0}\,|\,\hat{p}\,|\,u_{l,k_0}\rangle$

Matrix elements of the perturbed Hamiltonian from $k \cdot p$ (assuming 1D):

$$H_{nl}(k_0+q) = \langle u_{n,k_0}\,|\,\hat{H}(k_0+q)\,|\,u_{l,k_0}\rangle \approx \frac{\hbar}{m_0}qp_{nl,k_0} + \delta_{nl}\left[E_n(k_0) + \frac{\hbar^2qk_0}{m_0} + \frac{\hbar^2q^2}{2m_0}\right]$$

Perturbed eigenvalues: $$E_n(k_0+q) \approx E_n(k_0) + \frac{\hbar(\hbar k_0 + p_{nn,k_0})}{m_0}\,q + \frac{\hbar^2q^2}{2m_0}\left(1 + \frac{2}{m_0}\sum_{l\neq n}\frac{|p_{nl,k_0}|^2}{E_n - E_l}\right)$$

should be $1/m^*$

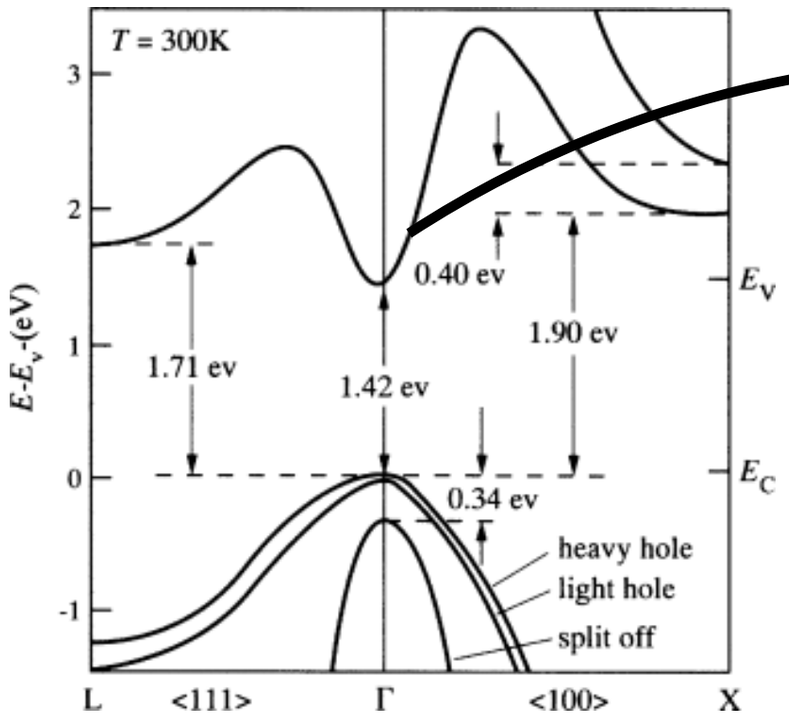
Effective mass (non-degenerate, 3D):

$$\frac{m_0}{m^*_{\alpha\beta,n,k_0}} = \delta_{\alpha\beta} + \frac{1}{m_0}\sum_{l\neq n}\frac{p^{(\alpha)}_{nl,k_0}p^{(\beta)}_{ln,k_0} + p^{(\beta)}_{nl,k_0}p^{(\alpha)}_{ln,k_0}}{E_{n,k_0} - E_{l,k_0}} \qquad \alpha,\beta = x,y,z \text{ (or } 1,\ 2,\ 3)$$

Book: Ashcroft and Mermin

Band gap issue

GaAs



$$\frac{m_0}{m_{\mathsf{c}}^*} \approx 1 + \frac{1}{m_0} \sum_{l \in \mathsf{h}} \frac{p_{\mathsf{c},l}^{(\alpha)} p_{l,\mathsf{c}}^{(\beta)} + p_{\mathsf{c},l}^{(\beta)} p_{l,\mathsf{c}}^{(\alpha)}}{E_{\mathsf{c}} - E_l}$$

$$\frac{m_0}{m_{\mathsf{c}}^*} \approx 1 + \frac{2(p_{\mathsf{hh,c}}^2 + p_{\mathsf{lh,c}}^2 + p_{\mathsf{so,c}}^2)}{m_0(E_{\mathsf{c}} - E_{\mathsf{v}})} = 1 + \frac{2p_{\mathsf{v,c}}^2}{m_0 E_g}$$

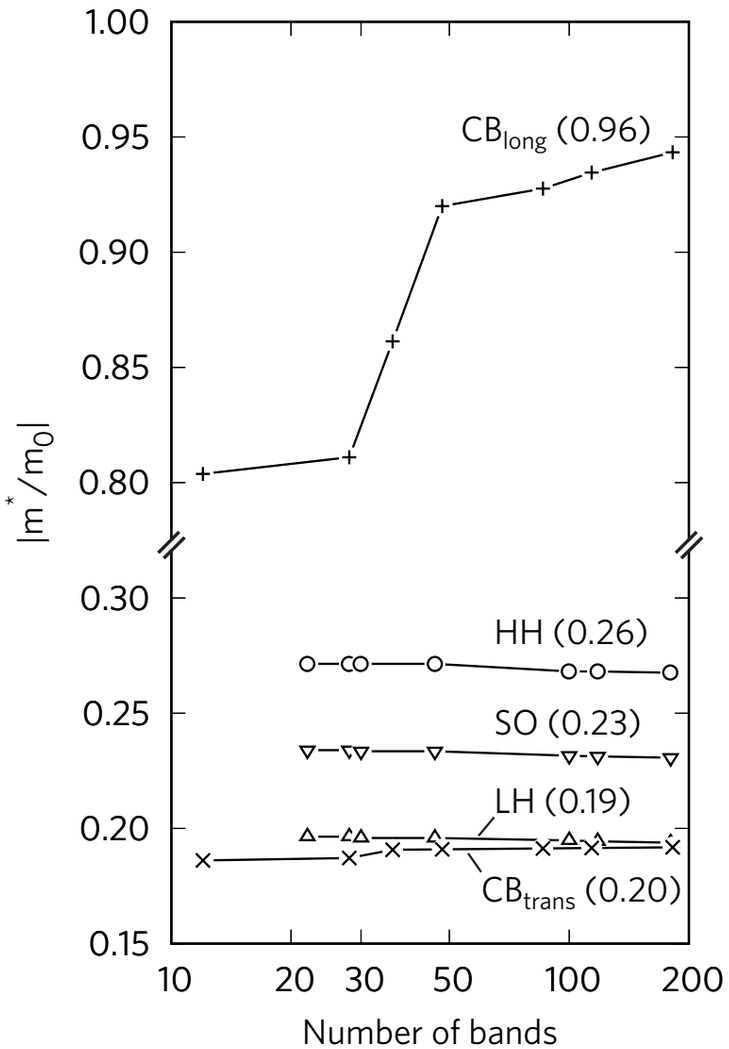
GGA-PBE band gap of GaAs: 0.4 eV

Kim *et al.* Phys. Rev. B **82**, 205212 (2010)

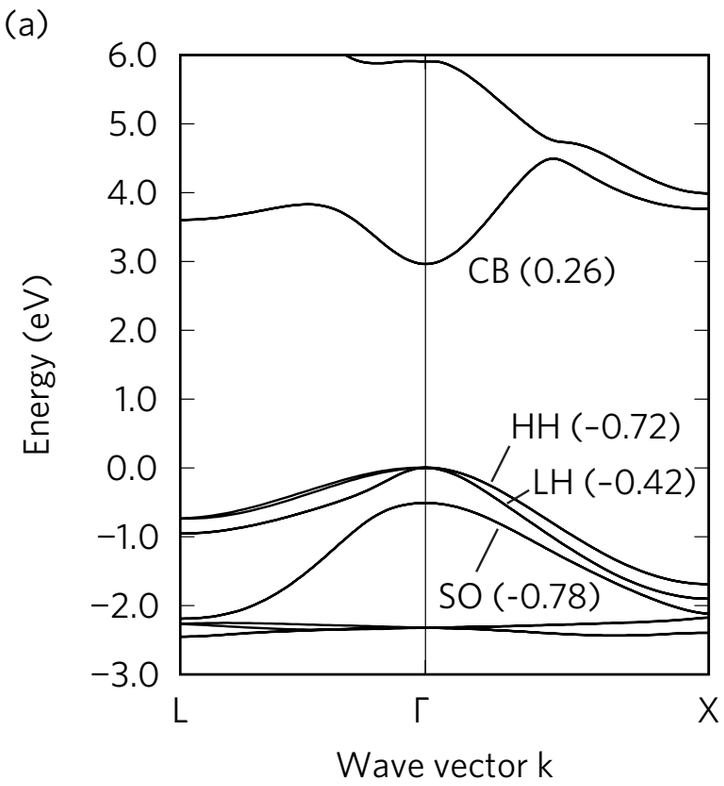
Element	Method	$\lvert m^*_{\text{electron}}/m_e \rvert$
GaAs	PBE	0.030
	$\text{MBJLDA}_{\text{bgfit}}$	0.090
	$\text{MBJLDA}_{\text{efmfit}}$	0.066
	$\text{HSE}_{\text{bgfit}}$	0.067
	Expt.	0.067

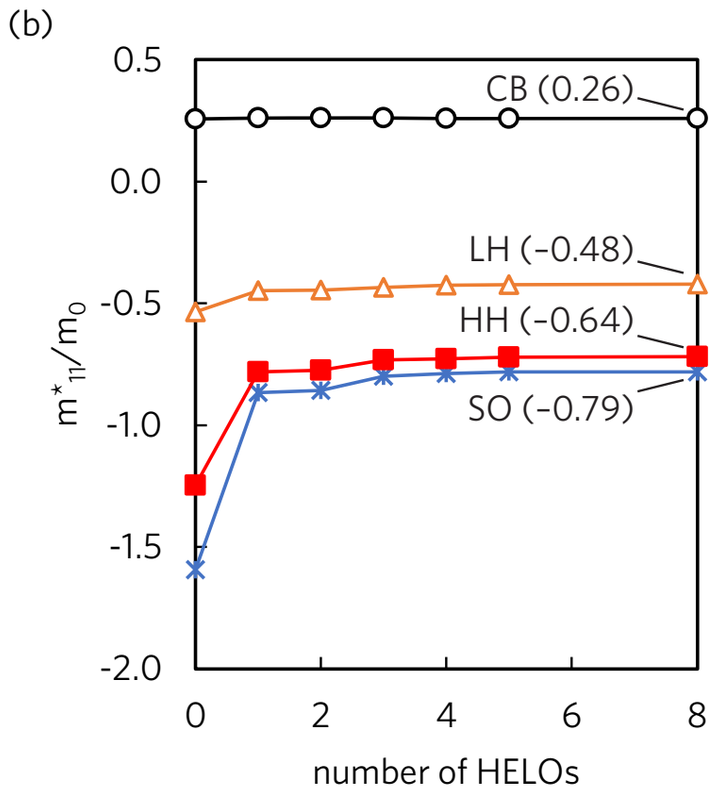
Finite sum over states issue

Si (s-p bonding)



CuI (Cu-d states)





- s-, p-, d-, f-LOs are added at high energy (~100 Ry)
- $\Delta l \pm 1$ rule for optical transitions
- Semicore and core states are also important
- GW calculations also "suffer" from the sum over states (e.g., ZnO, MoS_2)
- Sternheimer PT avoids $\sum_{l \neq n}$ (e.g., *Abinit* implementation)

Comp. Phys. Commun. **261**, 107648 (2021)

Implementation in WIEN2k (and VASP)

rubel75 / mstar

https://github.com/rubel75/mstar

README GPL-3.0 license

mstar

Effective mass calculation with DFT using a perturbation theory. Currently supported codes:

- WIEN2k
- VASP

It is written in Fortran and intended for Linux OS

Projects Wiki Security Insights Settings

Home

Oleg Rubel edited this page on Jul 9, 2020 · 8 revisions

Welcome to the `mstar` wiki!

- How to generate case.mommat2 file in WIEN2k
- How to generate WAVEDER file in VASP
- Tutorial: Si with SOC (WIEN2k)
- Tutorial: Si with SOC (VASP)

Workflow

(1) Standard SCF calculation

- SOC is important

(2) Expand number of bands (add HELOs). Recalculate DFT orbitals.

- Edit "case.in1(c)", increase E_{max} and execute "x lapw1"; edit "case.inso", increase E_{max} and execute "x lapwso"
- Alternatively, execute "x_nmr -mode in1 -nodes 3" and copy "case.in1(c)_nmr" as "case.in1(c)"; edit "case.inso", increase $E_{max} = 999$ Ry (get *all* eigenvalues), execute "x lapw1" and "x lapwso"

(3) Compute momentum matrix elements (same as for "optic")

- Get the template "case.inop", edit to enable writing of momentum matrix elements "OFF → ON", increase increase E_{max} to match the value set in "case.inso"
- Execute optic "x optic -so"; check presence of "case.mommat2*" files

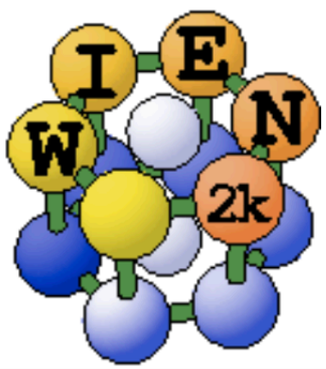
(4) Compute $[m_0/m^*_{\alpha\beta}]^{-1}$ tensor for each k-point and band index using "mstar"

- Execute mstar "/path/to/mstar case.mommat2up 1e-5" (here $\Delta E = 10^{-5}$ Ha is the search tolerance for degenerate states)
- Check output files "minv_ij-up.dat" ($m_0/m^*_{\alpha\beta,n,k_0}$ tensor), "minv_pr-up.dat" (principal components of the tensor), "minv_c-up.dat" (conductivity mass $m_0/\langle m^*_{n,k_0}\rangle_{\text{cond}}$), and "minv_d-up.dat" (density of states mass $m_0/\langle m^*_{n,k_0}\rangle_{\text{dos}}$)

Warning: Do not use with hybrid (%HF) functionals in WIEN2k

Demo “mstar” in WIEN2k (also offered as a tutorial)

Effective mass in Si from perturbation theory



\+ mstar

https://github.com/rubel75/mstar

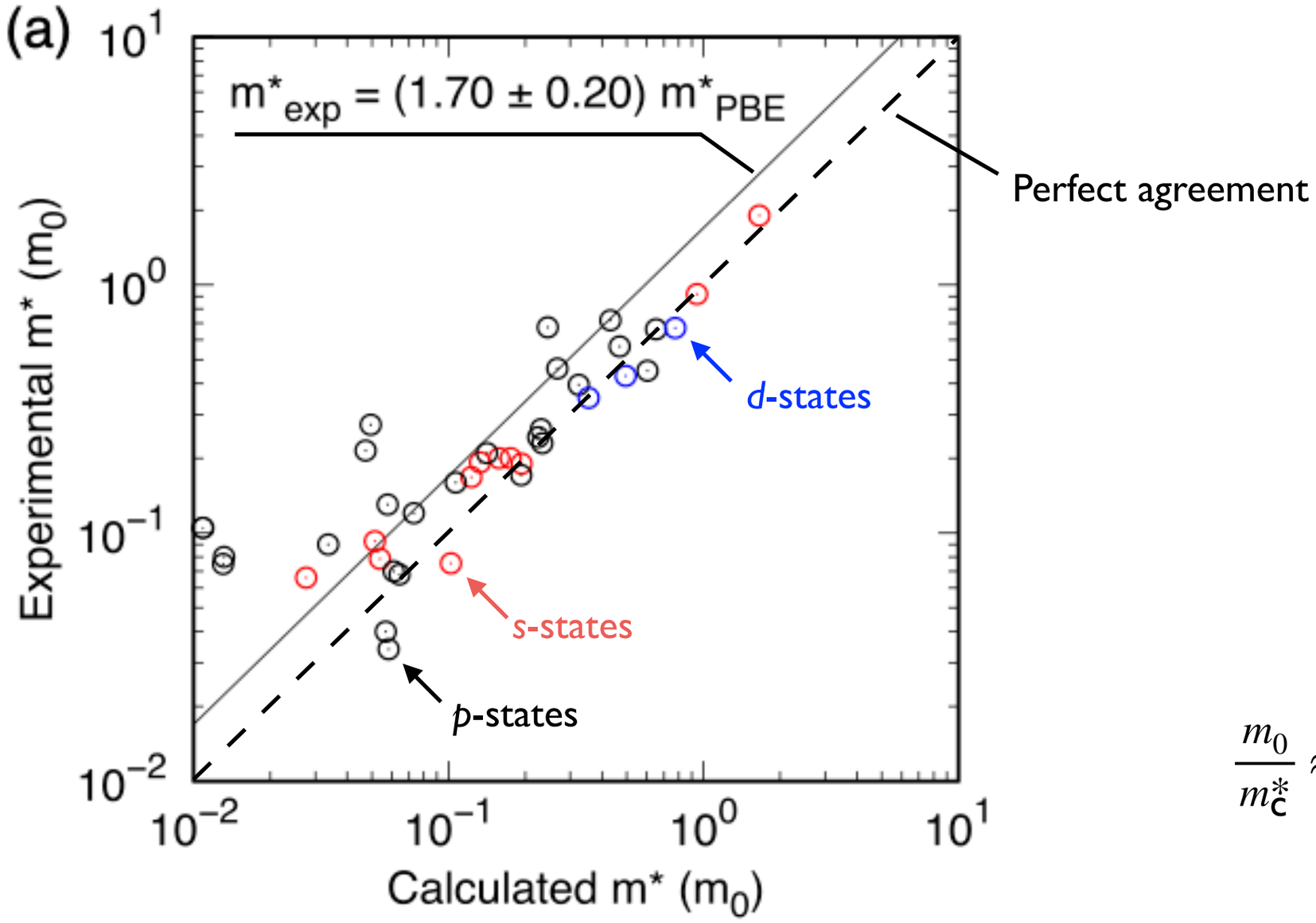
"mstar60" dataset

Benchmarking exchange-correlation potentials with the mstar60 dataset: Importance of the nonlocal exchange potential for effective mass calculations in semiconductors

Magdalena Laurien and Oleg Rubel
Phys. Rev. B **106**, 045204 – Published 15 July 2022

Si (227)	$m_{n,\perp}$ (CBM)
	$m_{n,\parallel}$ (CBM)
	$m_{p,\mathrm{hh}}$ (Γ) [100]
	$m_{p,\mathrm{lh}}$ (Γ) [100]
	$m_{p,\mathrm{so}}$ (Γ)
GaAs (216)	m_n (Γ)
	$m_{n,\perp}$ (X6)
	$m_{n,\parallel}$ (X6) †a
	$m_{n,\perp}$ (L6)
	$m_{n,\parallel}$ (L6)
	$m_{p,\mathrm{hh}}$ (Γ) [100]
	$m_{p,\mathrm{lh}}$ (Γ) [100]
	$m_{p,\mathrm{so}}$ (Γ)
GaN (186)	$m_{n,\parallel}$ (Γ)
	$m_{n,\perp}$ (Γ)
InP (216)	m_n (Γ)
	$m_{p,\mathrm{hh}}$ (Γ) [100]
	$m_{p,\mathrm{lh}}$ (Γ) [100]
	$m_{p,\mathrm{so}}$ (Γ)
CdS (186)	$m_{n,\perp}$ (Γ, A exciton)
	$m_{n,\parallel}$ (Γ, A exciton)
	$m_{p,\perp}$ (Γ, A exciton)
	$m_{p,\parallel}$ (Γ, A exciton) †a
CdTe (216)	m_n (Γ)
	$m_{p,\mathrm{lh}}$ [100] (Γ)
	$m_{p,\mathrm{hh}}$ [100] (Γ)
PbS (225)	$m_{n,\perp}$ (L)
	$m_{n,\parallel}$ (L)
	$m_{p,\perp}$ (L)
	$m_{p,\parallel}$ (L)
PbSe (225)	$m_{n,\perp}$ (L)
	$m_{n,\parallel}$ (L)
	$m_{p,\perp}$ (L)
	$m_{p,\parallel}$ (L)
PbTe (225)	$m_{n,\perp}$ (L)
	$m_{n,\parallel}$ (L)
	$m_{n,\perp}$ (L)
	$m_{p,\parallel}$ (L)
SiC (216)	$m_{n,\parallel}$ (X)
	$m_{n,\perp}$ (X)
	m_p (Γ) [100]
BN [70] (194)	m_p ($\bar{\mathrm{K}}$, $\bar{\Gamma}$-$\bar{\mathrm{K}}$ direction) †a
bP (64)	m_n (Y) [010]
	m_n (Y) [001]
	m_n (Y) [100]
	m_p (Y) [010]
	m_p (Y) [001]
MoS_2 [73] (194)	m_p ($\bar{\Gamma}$, $\bar{\Gamma}$-$\bar{\mathrm{K}}$ direction)
WS_2 (194)	m_p ($\bar{\mathrm{K}}$, $\bar{\Gamma}$-$\bar{\mathrm{K}}$ direction)
	$m_{p,\mathrm{VB}-1}$ ($\bar{\mathrm{K}}$, $\bar{\Gamma}$-$\bar{\mathrm{K}}$ direction)
1L MoS_2	m_p (Γ, Γ-K direction)
	m_p (K, Γ-K direction)
	m_n (K)
1L $MoSe_2$	m_p (K, Γ-K direction)
	m_n (K)
1L WS_2	m_p ($\bar{\Gamma}$, $\bar{\Gamma}$-$\bar{\mathrm{K}}$ direction)
	m_p ($\bar{\mathrm{K}}$, $\bar{\Gamma}$-$\bar{\mathrm{K}}$ direction)
	$m_{p,\mathrm{so}}$ ($\bar{\mathrm{K}}$, $\bar{\Gamma}$-$\bar{\mathrm{K}}$ direction)
1L WSe_2	m_p (Γ, Γ-K direction)

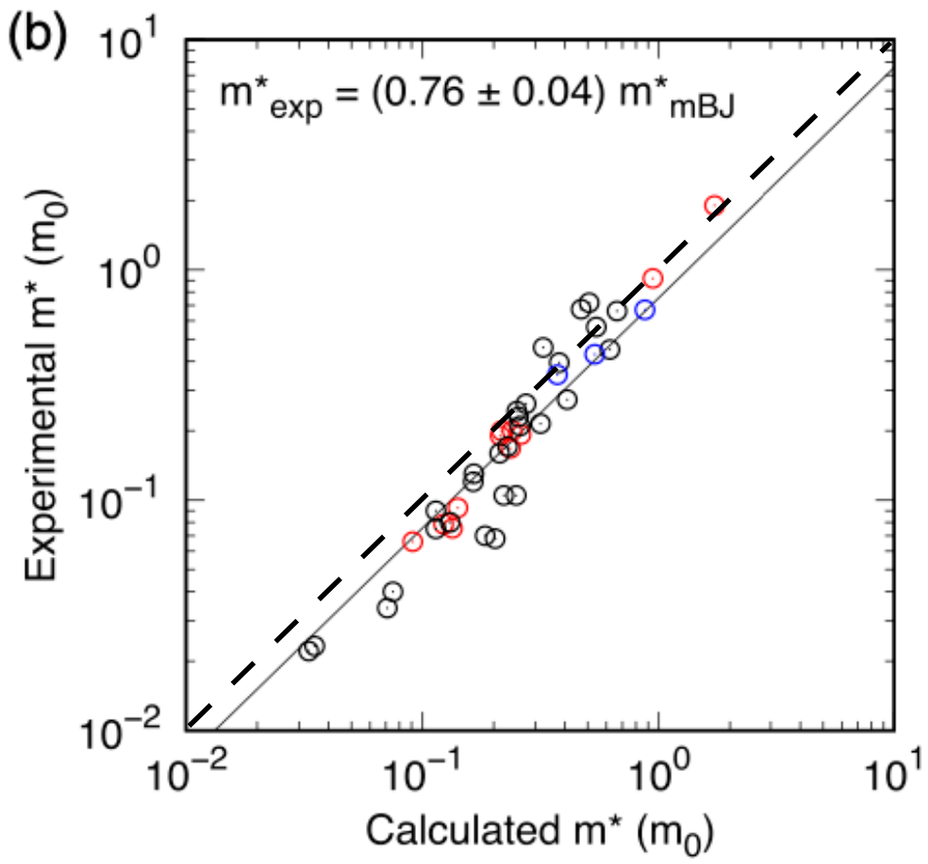
GGA-PBE m* are underestimated



$$\frac{m_0}{m^*_{\mathbf{c}}} \approx = 1 + \frac{2p^2_{\mathbf{v,c}}}{m_0 E_g}$$

Phys. Rev. B **106**, 045204 (2022)

mBJ m* are (slightly) overestimated

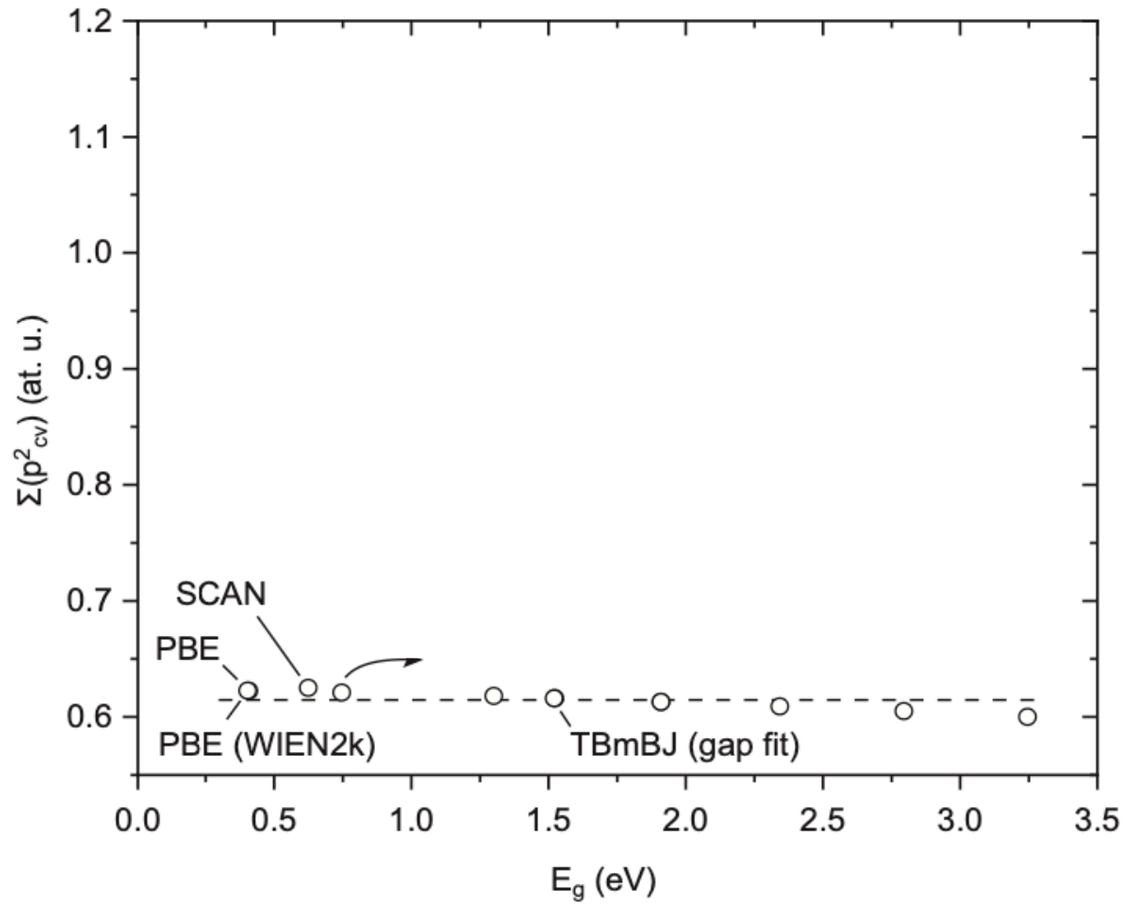


Kim *et al.* Phys. Rev. B **82**, 205212 (2010)

Element	Method	$\lvert m^*_{\text{electron}}/m_e \rvert$
GaAs	PBE	0.030
	$\text{MBJLDA}_{\text{bgfit}}$	0.090
	$\text{MBJLDA}_{\text{efmfit}}$	0.066
	$\text{HSE}_{\text{bgfit}}$	0.067
	Expt.	0.067

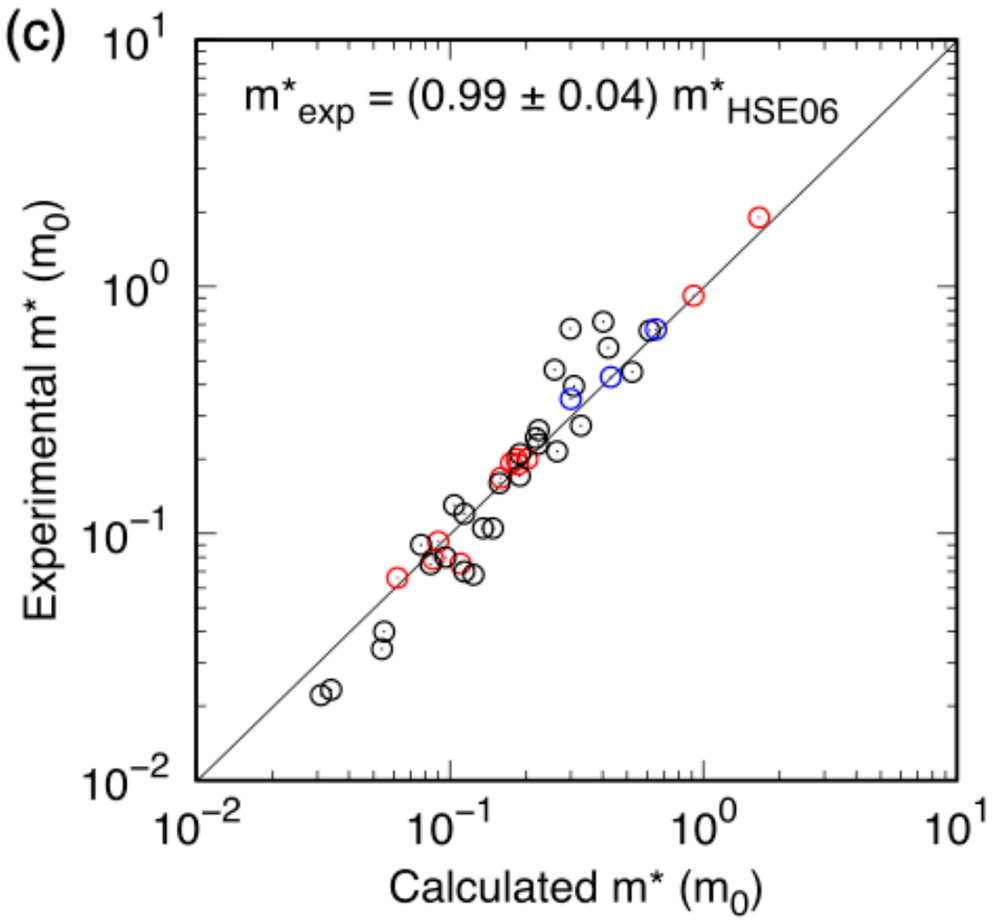
$$\frac{m_0}{m^*_{\mathbf{c}}} \approx = 1 + \frac{2p^2_{\mathbf{v,c}}}{m_0\, E_g}$$

Momentum matrix element $\sum p^2_{\mathbf{c,v}}$ for GaAs



Phys. Rev. B **106**, 045204 (2022)

HSE06 m* show best agreement with experiment



Kim *et al.* Phys. Rev. B **82**, 205212 (2010)

Element	Method	$\lvert m^*_{\text{electron}}/m_e \rvert$
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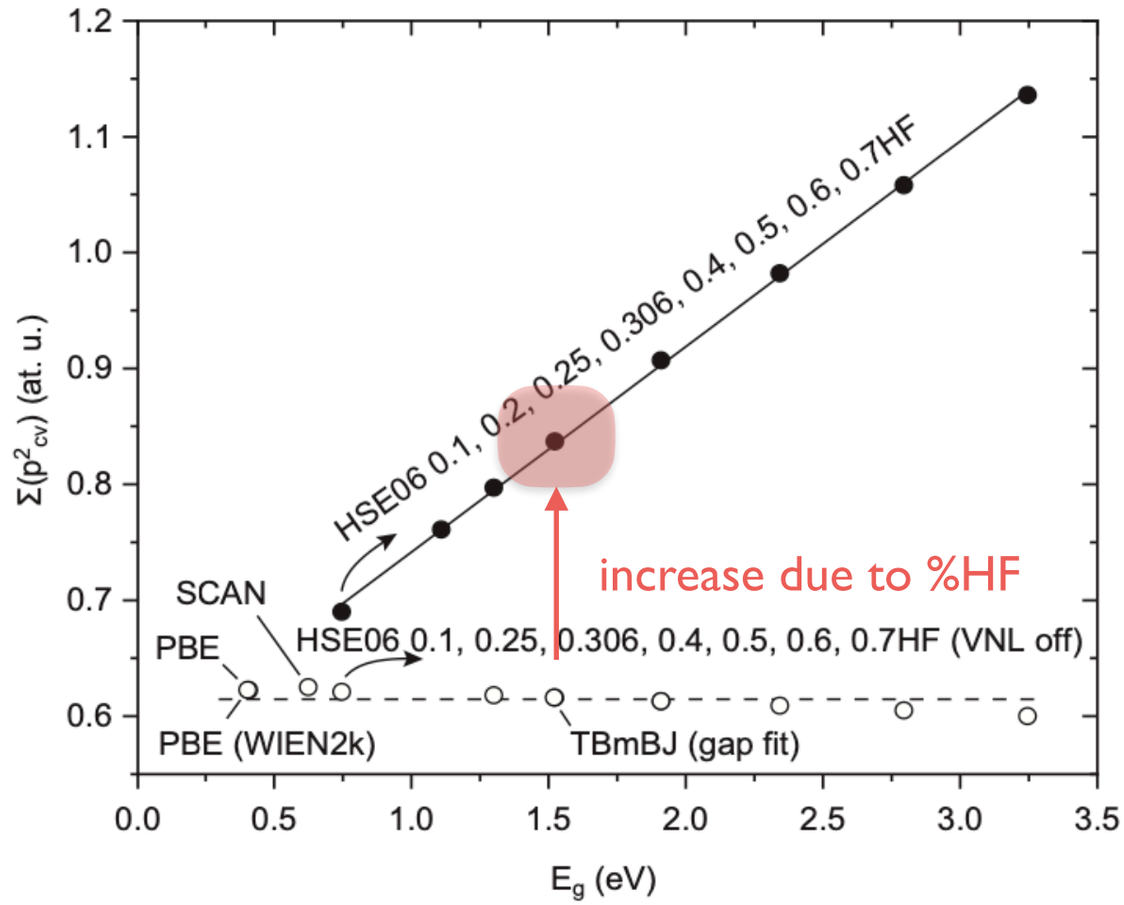
	$\text{HSE}_{\text{bgfit}}$	0.067
	Expt.	0.067

$$\frac{m_0}{m^*_{\mathbf{c}}} \approx = 1 + \frac{2m_0 v^2_{\mathbf{v,c}}}{E_g}$$

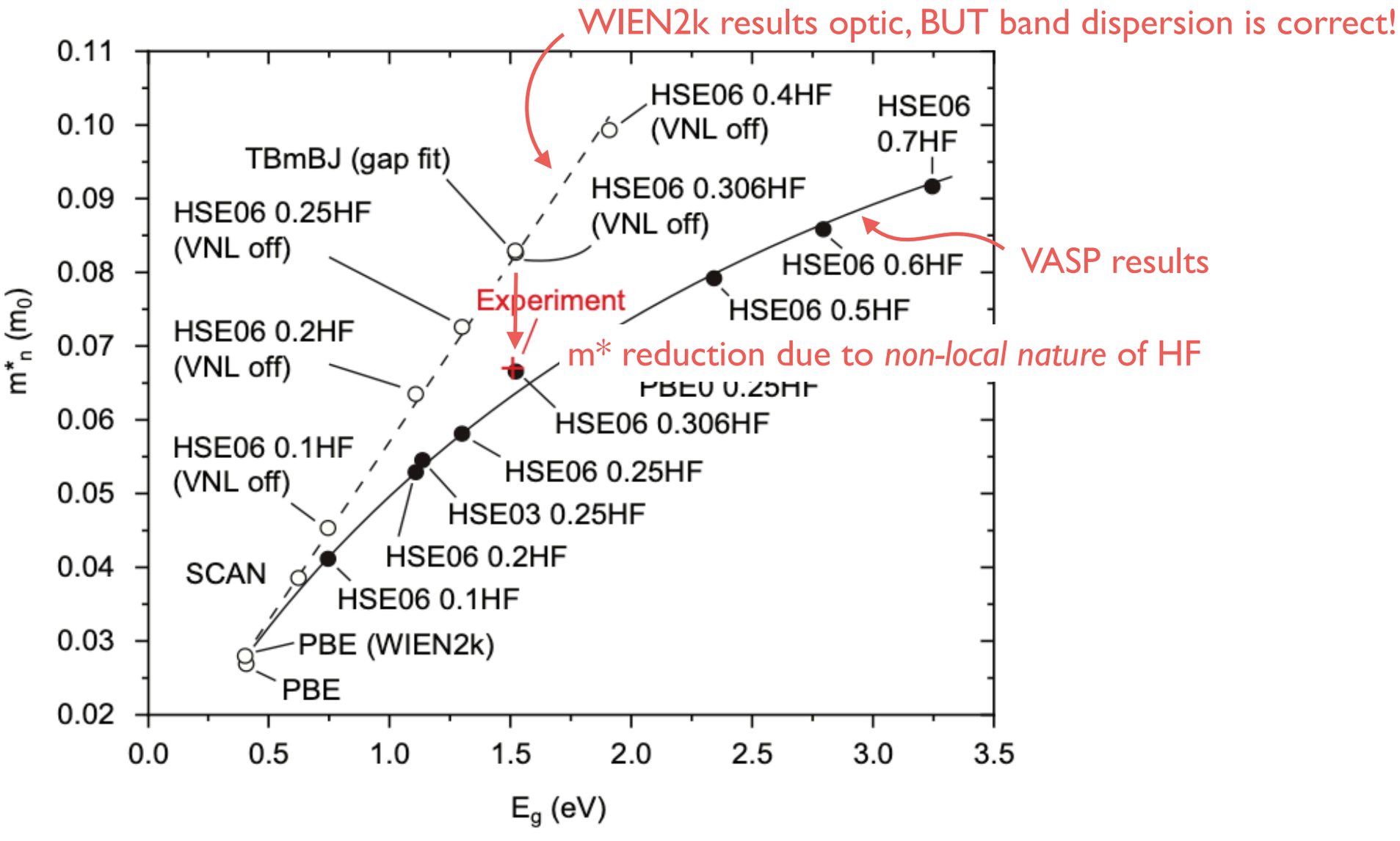
$v^2 \neq p^2$ *velocity* matrix element



Phys. Rev. B **106**, 045204 (2022)

HSE06 m* from PT for GaAs with varied %HF

$$E_{xc}^{HSE} = aE_x^{HF,SR}(\omega) + (1-a)E_x^{PBE,SR}(\omega) + E_x^{PBE,LR}(\omega) + E_c^{PBE},$$



Phys. Rev. B **106**, 045204 (2022)

Additional contribution due to non-local potential

Schrödinger equation with a *local* potential

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

LDA, GGA, mBJ, SCAN

$$\hat{v} = \frac{i}{\hbar}[\hat{H}, \mathbf{r}] = \frac{\hat{p}}{m_0}$$

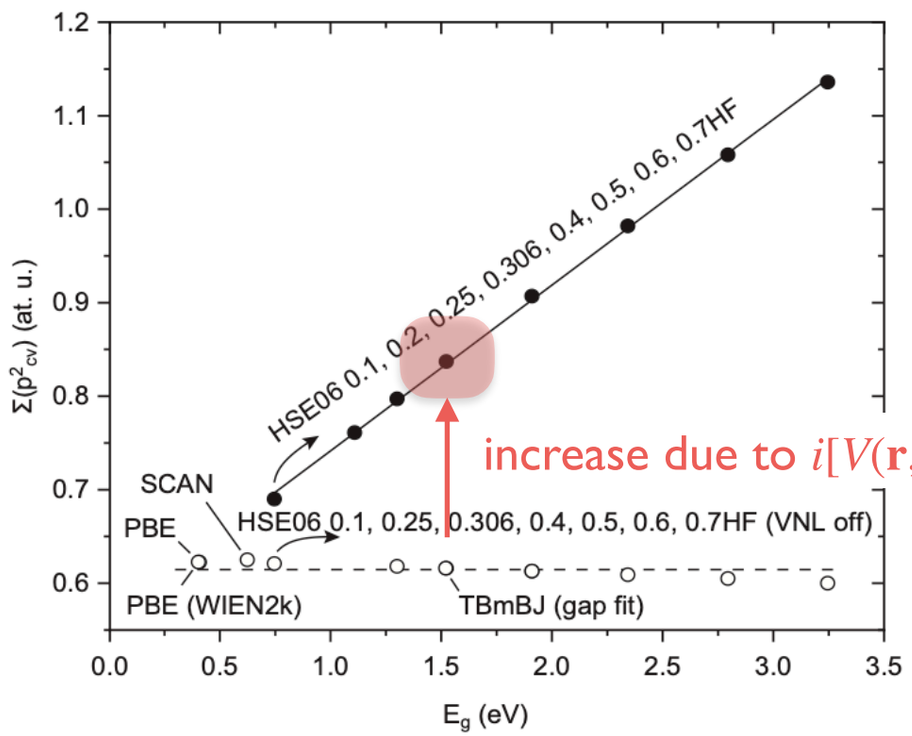
Schrödinger equation with a *non-local* potential

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + \int V(\mathbf{r}, \mathbf{r}')\psi(\mathbf{r}')\ d\mathbf{r}' = E\psi(\mathbf{r})$$

Hartree-Fock exchange (spinless), also GW:

$$-\int \left[\sum_j \frac{\psi_j^*(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \right] \psi_i(\mathbf{r}')\ d\mathbf{r}'$$

$$\hat{v} = \frac{i}{\hbar}[\hat{H}, \mathbf{r}] = \frac{\hat{p}}{m_0} + \frac{i}{\hbar}[V(\mathbf{r}, \mathbf{r}'), \mathbf{r}]$$

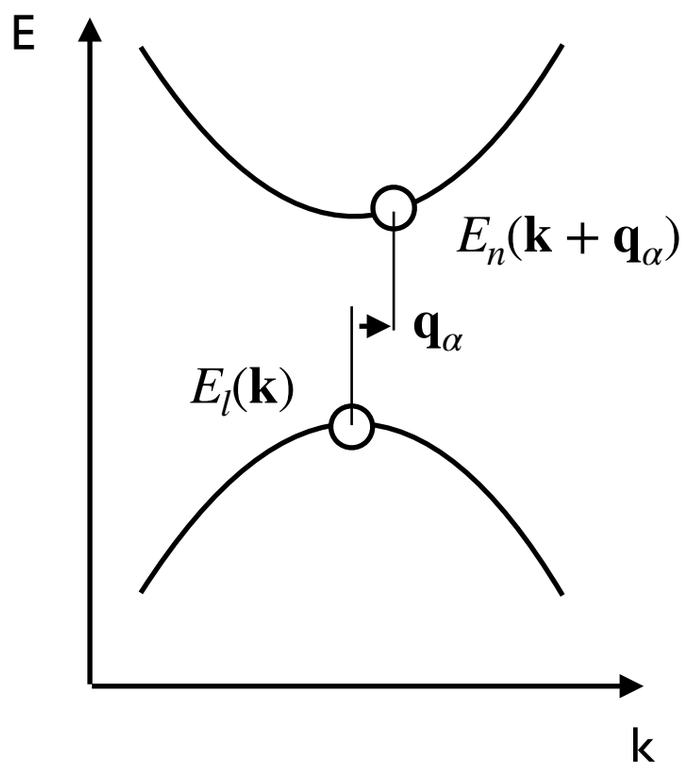


increase due to $i[V(\mathbf{r}, \mathbf{r}'), \mathbf{r}]/\hbar$

Does it mean that the "true" XC potential should be non-local?

Open question: Why $\sum v_{c,v}^2 > \sum p_{c,v}^2$?

Proper $\hat{v}$ matrix elements in WIEN2k



Length gauge matrix elements [Asahi *et al.*, Phys. Rev. B 59, 7486 (1999)]:

$$v_{nl}^{(\alpha)} \approx \frac{1}{q} \langle u_{\mathbf{k},l} \,|\, u_{\mathbf{k}+\mathbf{q}_\alpha,n} \rangle \, [E_n(\mathbf{k}+\mathbf{q}_\alpha) - E_l(\mathbf{k})] \quad \text{for } \textbf{very} \text{ small } q$$

$\langle u_{\mathbf{k},l} \,|\, u_{\mathbf{k}+\mathbf{q}_\alpha,n} \rangle$ from wien2wannier

GaAs

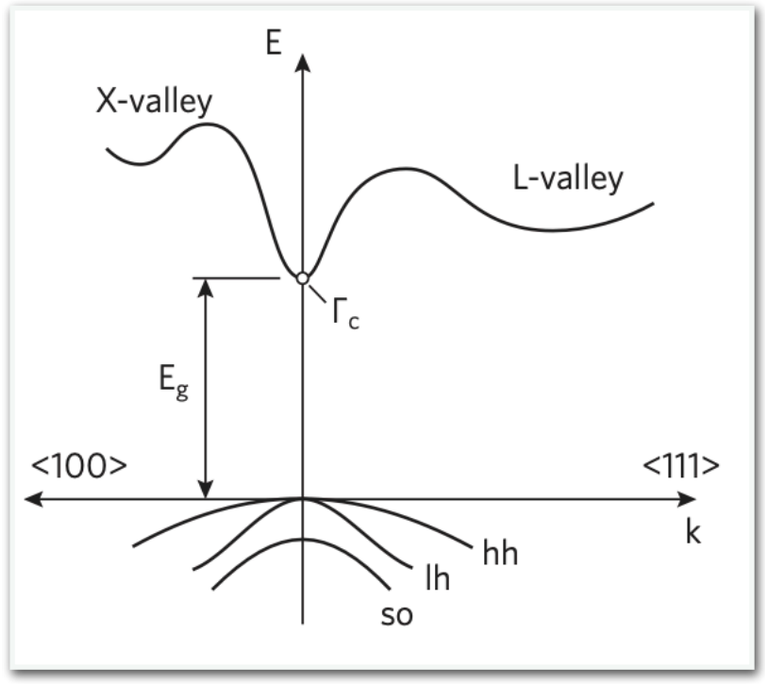


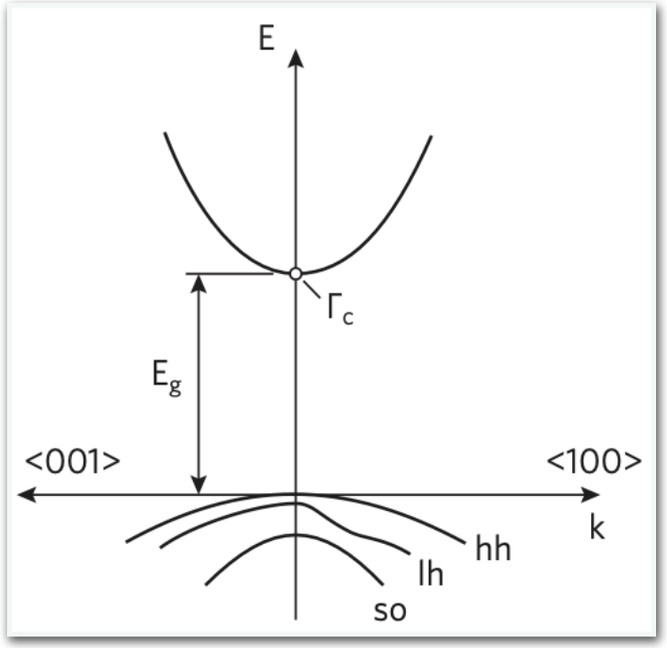
Table 3. Length-gauge $|v_{mn}^{(x)}|^2$ and velocity-gauge $|p_{mn}^{(x)}|^2$ matrix elements (at.u.) in GaAs calculated using WIEN2k (with YSH) and VASP (with HSE06). Due to the non-local potential the velocity and the length gauges are *not* identical. The band degeneracy is given as a superscript in parentheses and the subscripts are explained in Figure 2a. The logarithmic deviation between $\sum |p_{vc}^{(x)}|^2$ and $\sum |v_{vc}^{(x)}|^2$ is given in parentheses (Δ as per Equation (10)).

Transition	$\sum \lvert v_{mn}^{(x)} \rvert^2$		$\sum \lvert p_{mn}^{(x)} \rvert^2$
	WIEN2k	VASP	
$\Gamma_{lh,hh}^{(\times 4)} - \Gamma_c^{(\times 2)}$	0.534	0.541	0.420
$\Gamma_{so}^{(\times 2)} - \Gamma_c^{(\times 2)}$	0.255	0.256	0.208
Total	0.789 (+23%)	0.797	0.628

Computation **10**, 22 (2022)

Other materials

GaN



GaN

Transition	$\sum \lvert v_{mn}^{(x)} \rvert^2$	$\sum \lvert v_{mn}^{(z)} \rvert^2$	$\sum \lvert p_{mn}^{(x)} \rvert^2$	$\sum \lvert p_{mn}^{(z)} \rvert^2$
$\Gamma_{hh}^{(\times 2)} - \Gamma_c^{(\times 2)}$	0.211	0	0.183	0
$\Gamma_{lh}^{(\times 2)} - \Gamma_c^{(\times 2)}$	0.256	0.055	0.163	0.042
$\Gamma_{so}^{(\times 2)} - \Gamma_c^{(\times 2)}$	0.026	0.507	0.018	0.377
Total	0.493 (+30%)	0.562 (+29%)	0.364	0.419

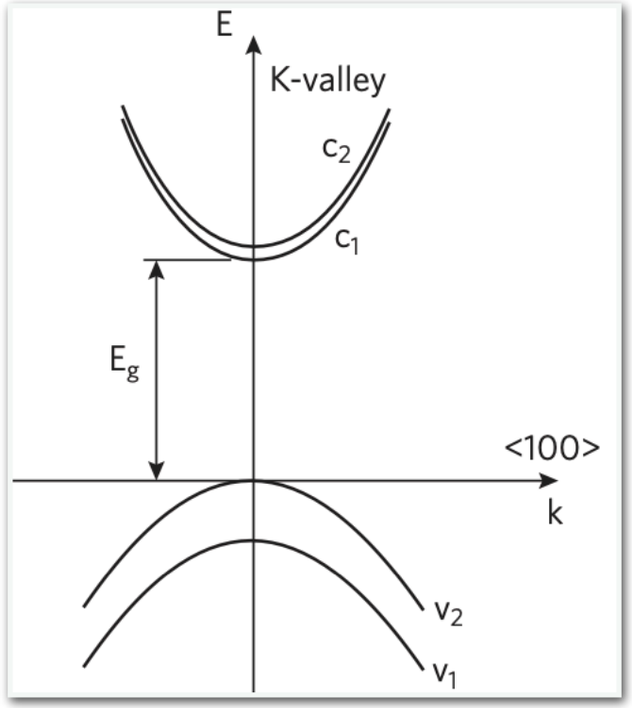
Monolayer MoS_2

Transition	$\sum \lvert v_{mn}^{(x)} \rvert^2$	$\sum \lvert p_{mn}^{(x)} \rvert^2$
$K_{v_1} - K_{c_1}$	0	0
$K_{v_2} - K_{c_1}$	0.107	0.075
$K_{v_1} - K_{c_2}$	0.106	0.074
$K_{v_2} - K_{c_2}$	0	0
Total	0.213 (+36%)	0.149

$(CH_3NH_3)PbI_3$

Transition	$\sum \lvert v_{mn}^{(x,y,z)} \rvert^2$	$\sum \lvert p_{mn}^{(x,y,z)} \rvert^2$
$R_v^{(\times 2)} - R_c^{(\times 2)}$	0.195, 0.150, 0.128 (+11, +11, +8%) [a]	0.174, 0.135, 0.118

Monolayer MoS_2



$|v|^2$ enhancement = stronger optical transitions & more efficient dielectric screening

Computation **10**, 22 (2022)

Summary

- Computing the full tensor $m^*_{\alpha\beta}$ by polynomial fitting can be non-trivial
- "mstar" gives access to the full tensor $m^*_{\alpha\beta}$ via perturbation theory (all *k*-points, all bands)
- The perturbation sum converges slowly (especially with *d*-electrons at the band edges)

- GGA-PBE masses are generally too light (E_g error)
- mBJ masses are somewhat heavier (low $p^2_{c,v}$)
- Hybrid (PBE + %HF) masses are most accurate (improved $v^2_{c,v} > p^2_{c,v}$ due to non-locality of the XC potential)
- WIEN2k can compute velocity matrix elements (incl. non-locality of the XC potential) via a finite difference (~30% correction for $v^2_{c,v}$)

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