Fundamental gap problem in density-functional theory

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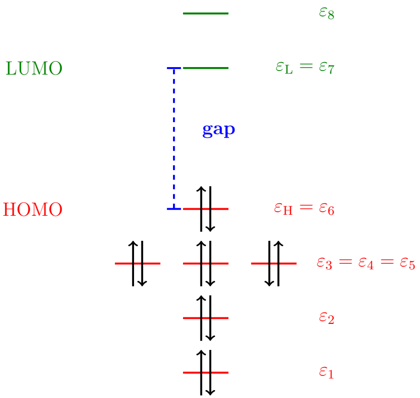
Molecular orbital energy diagram and gaps



- The HOMO-LUMO gap can be interpreted in two ways.
- $\varepsilon_\mathrm{L} - \varepsilon_\mathrm{H} = \left(E_0^{N+1} - E_0^N\right) + \left(E_0^{N-1} - E_0^N\right) = E_\mathrm{g}$ ← fundamental gap [charged excitations]
- $\varepsilon_\mathrm{L} - \varepsilon_\mathrm{H} = E_1^N - E_0^N = \omega_\mathrm{g}$ ← optical gap [neutral excitation]

Limitations of the one-electron picture

Materials Horizons

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Mind the gap!

Jean-Luc Bredas[ab]

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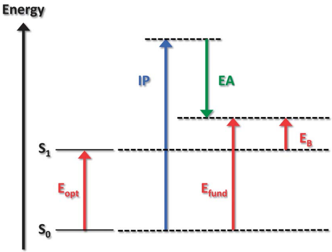
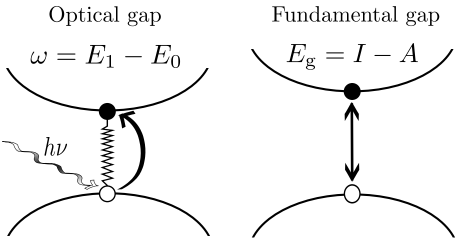


Fig. 1 Illustration of gap energies in the molecular case: S_0 denotes the (singlet) electronic ground state and S_1 the lowest (singlet) excited state (considered here to be accessible *via* one-photon absorption). The $S_1 - S_0$ energy difference then corresponds to the optical gap E_{opt}. The magnitude of the ionization potential is given by the blue vertical line and the magnitude of the electron affinity by the green vertical line; the IP − EA difference represents the fundamental gap, E_{fund}. The electron–hole pair binding energy, E_B, is given by $E_{fund} - E_{opt}$.



Optical gap

$$\omega = E_1 - E_0$$

Fundamental gap

$$E_g = I - A$$

Courtesy of B. Senjean

Many-body problem in density-functional theory

- In quantum mechanics, the ground-state N-electron electronic repulsion energy is expressed (in atomic units) as follows,

$$W_{\rm ee} = \frac{N(N-1)}{2}\int_{\mathbb{R}^3}{\rm d}\mathbf{r}_1\int_{\mathbb{R}^3}{\rm d}\mathbf{r}_2\int_{\mathbb{R}^3}{\rm d}\mathbf{r}_3\ldots\int_{\mathbb{R}^3}{\rm d}\mathbf{r}_N\,\frac{\left|\Psi_0(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N)\right|^2}{|\mathbf{r}_1-\mathbf{r}_2|},$$

  where $\Psi_0(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N)$ is the N-electron ground-state wave function.

- In DFT, $W_{\rm ee}$ is determined from the ground-state N-electron density $n_0^N(\mathbf{r})$, which is a much simpler mathematical object than the ground-state wave function.

- For that purpose, the so-called Hartree-exchange-correlation (Hxc) density functional has been introduced by Kohn and Sham (KS),

$$W_{\rm ee} \leftarrow E_{\rm Hxc}\left[n\right]\Big|_{n=n_0^N},$$

  where the density is determined exactly from the KS orbitals as follows,

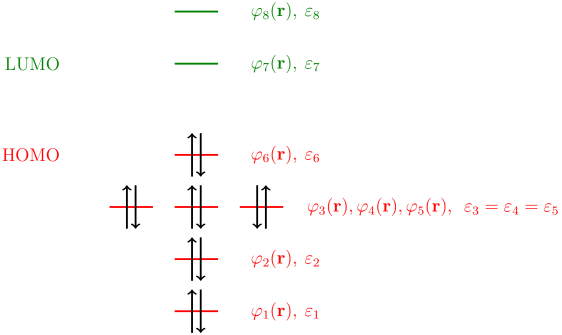
$$n_0^N(\mathbf{r}) = \sum_{i=1}^{N}\left|\varphi_i(\mathbf{r})\right|^2.$$

- Self-consistent equations fulfilled by the KS orbitals:

$$-\frac{1}{2}\nabla^2_{\mathbf{r}}\varphi_i(\mathbf{r}) + \left[v_{\rm ext}(\mathbf{r}) + \frac{\delta E_{\rm Hxc}\left[n_0^N\right]}{\delta n(\mathbf{r})} \right] \times \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}),$$

  where $v_{\rm ext}(\mathbf{r})$ is any external local (multiplicative) interaction potential energy (the nuclear-electron attraction potential for example) at position $\mathbf{r}$.

- The additional Hxc potential $\delta E_{\rm Hxc}\left[n_0^N\right]/\delta n(\mathbf{r})$ ensures that the density of the true system is recovered, in principle exactly, from the KS orbitals.



Concept of band structure

PHYSICAL REVIEW B **93**, 205205 (2016)

More realistic band gaps from meta-generalized gradient approximations: Only in a generalized Kohn-Sham scheme

Zeng-hui Yang, Haowei Peng, Jianwei Sun, and John P. Perdew
Department of Physics, Temple University, Philadelphia, Pennsylvania 19122, USA

(Received 1 March 2016; revised manuscript received 6 May 2016; published 24 May 2016)

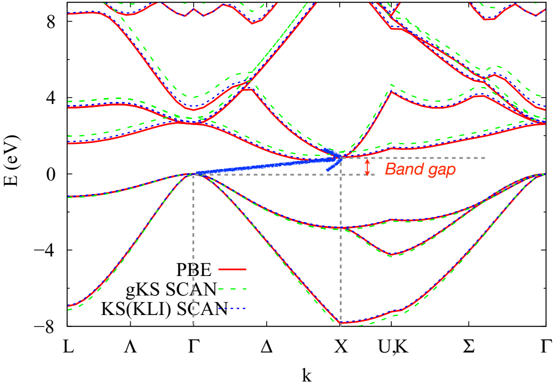


FIG. 3. The band structure of Si calculated with PBE, gKS SCAN, and KS(KLI) SCAN.

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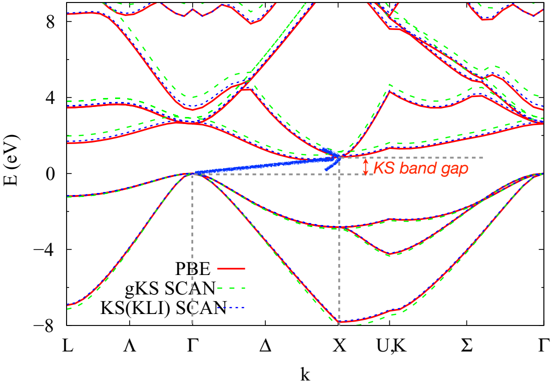

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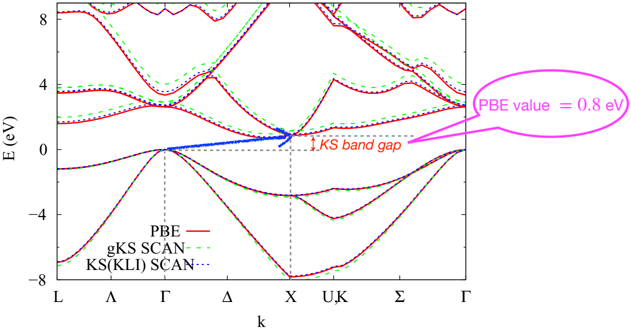
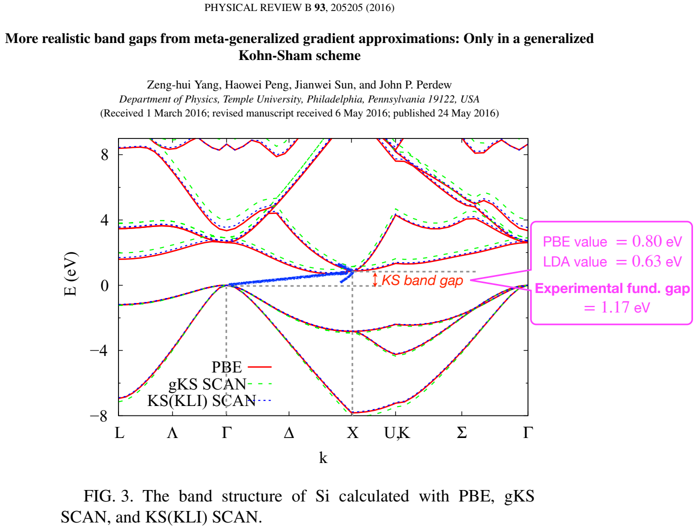


KS band gap

PBE value $= 0.8$ eV

FIG. 3. The band structure of Si calculated with PBE, gKS SCAN, and KS(KLI) SCAN.

Concept of band structure



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PBE value $= 0.80$ eV
LDA value $= 0.63$ eV

Experimental fund. gap
$= 1.17$ eV

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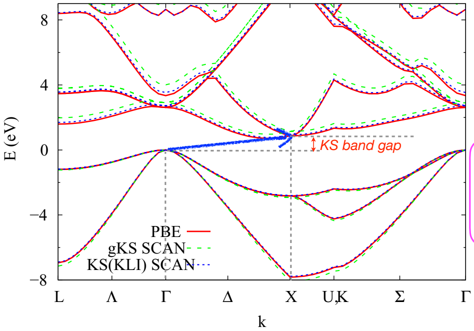


PBE value $= 0.80$ eV
LDA value $= 0.63$ eV

Experimental fund. gap
$= 1.17$ eV

Accurate KS gap*
$= 0.82$ eV

FIG. 3. The band structure of Si calculated with PBE, gKS SCAN, and KS(KLI) SCAN.

*A. Aouina, "A novel shortcut for computational materials design", PhD thesis, February 2022.

Concept of band structure

*The exact KS gap is actually **not** supposed to match the exact fundamental gap!*

N-centered ensemble DFT

- Let us introduce the so-called N-centered ground-state *ensemble energy* E_0^{ξ}:

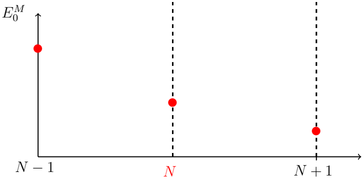
$$E_0^{\xi} = \xi E_0^{N-1} + \xi E_0^{N+1} + \Big(1-2\xi\Big) E_0^{N}, \quad \text{where} \;\; 0 \leq \xi \leq 1/2.$$

- E_0^{ξ} is *linear* in ξ and its slope is equal to the *fundamental gap*.
- The N-centered ensemble energy is a *functional* of the N-centered ensemble *density*

$$n_0^{\xi}(\mathbf{r}) \quad = \quad \xi n_0^{N-1}(\mathbf{r}) + \xi n_0^{N+1}(\mathbf{r}) + \Big(1-2\xi\Big) n_0^{N}(\mathbf{r}),$$

which, by construction, integrates to N for any ξ, hence the name "N-centered".

- Conventional (N-electron) DFT is recovered when $\xi = 0$ i.e. $\boxed{E_{\rm Hxc}^{\xi}[n] \overset{\xi=0}{\rightarrow} E_{\rm Hxc}[n]}$.



integral number M of electrons

B. Senjean and E. Fromager, Phys. Rev. A **98**, 022513 (2018).

Derivative discontinuity

- It has been known for a long time that the true (interacting) and KS gaps *do not match*[1,2,6].

- This fact appears (more) explicitly within the N-centered ensemble DFT formalism [3−6]:

$$E_{\rm g} = \left(\varepsilon_{\rm L}^{\rm KS} + \underbrace{\left.\frac{\partial E_{\rm Hxc}^{\xi}\left[n_0^N\right]}{\partial \xi}\right|_{\xi=0}}_{\textit{derivative discontinuity}}\right) - \varepsilon_{\rm H}^{\rm KS} \quad \equiv \quad \tilde{\varepsilon}_{\rm L}^{\rm KS} - \varepsilon_{\rm H}^{\rm KS}.$$

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[1] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. 49, 1691 (1982).

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[3] B. Senjean and E. Fromager, Phys. Rev. A **98**, 022513 (2018).

[4] B. Senjean and E. Fromager, Int. J. Quantum Chem. 2020; **120**:e26190.

[5] M. J. P. Hodgson, J. Wetherell, and E. Fromager, Phys. Rev. A **103**, 012806 (2021).

[6] F. Cernatic, B. Senjean, V. Robert, and E. Fromager, *Top Curr Chem (Z)* **380**, 4 (2022).

Proof: Lieb maximization in N-centered ensemble DFT

$$\boxed{\forall v, \quad E_0^{\lambda,\xi}[v] = \min_n \left\{ F^{\lambda,\xi}[n] + \int d\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r}) \right\}}$$

$$\Leftrightarrow \forall v, \forall n, \quad E_0^{\lambda,\xi}[v] \leq F^{\lambda,\xi}[n] + \int d\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r})$$

$$\Leftrightarrow \forall v, \forall n, \quad F^{\lambda,\xi}[n] \geq E_0^{\lambda,\xi}[v] - \int d\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r})$$

$$\Leftrightarrow \boxed{\forall n, \quad F^{\lambda,\xi}[n] = \max_v \left\{ E_0^{\lambda,\xi}[v] - \int d\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r}) \right\}}$$

- If $v^{\lambda,\xi}[n]$ is the maximizing potential then $\dfrac{\partial F^{\lambda,\xi}[n]}{\partial \xi} = \left.\dfrac{\partial E_0^{\lambda,\xi}[v]}{\partial \xi}\right|_{v=v^{\lambda,\xi}[n]} = E_{\rm g}^{\lambda,\xi}[n]$ is nothing but a *density-functional fundamental gap*.
- When considering the conventional KS-DFT limit ($\xi = 0$) we obtain

$$\begin{aligned} E_{\rm g} &= E_{\rm g}^{\lambda=1,\xi=0}\left[n_0^N\right] = E_{\rm g}^{\lambda=0,\xi=0}\left[n_0^N\right] + \left(E_{\rm g}^{\lambda=1,\xi=0}\left[n_0^N\right] - E_{\rm g}^{\lambda=0,\xi=0}\left[n_0^N\right]\right) \\ &= \boxed{\varepsilon_{\rm L}^{\rm KS} - \varepsilon_{\rm H}^{\rm KS} + \left.\frac{\partial E_{\rm Hxc}^{\xi}\left[n_0^N\right]}{\partial \xi}\right|_{\xi=0} = E_{\rm g}} \end{aligned}$$

B. Senjean and E. Fromager, Phys. Rev. A **98**, 022513 (2018).