Species Dependent Scissor Shifts

Nelson Yeung
Nicholas Hine

April 11, 2019

1 Scissor Hamiltonian

The scissor hamiltonian allows one to apply species-dependent and subspace-dependent energy-level shifts to the hamiltonian, which has the effect of shifting eigenvalues associated with specific layers of the material. One can separately shift the valence and conduction subspaces associated with each layer. This also affects the total energy, so must be applied with great care if you are using the total energy for any purpose. The idea is that a band-alignment correction can be applied to the individual layers of non-covalently-bonded layered materials, though there may well be many other applications as well. It would seem "unwise" at best to apply this approach to different regions of the same molecule or solid which are strongly bonded: results would be unpredictable and likely unphysical. One ideal use would be to correct the alignment of the band-edges of a layered material heterobilayer so that the appropriate heterostructure type was realised, for example straddled-gap rather than broken-gap, using shifts chosen by reference to beyond-DFT accuracy calculations of the individual materials, or from experimental techniques such as ARPES.

In order to apply this shift, we define a scissor Hamiltonian operator as follows:

$$\hat{H}_{\text{scissor}} = |\phi_\eta\rangle K^{\eta\delta}_{\text{shifted}} \langle\phi_\delta| \, , \tag{1}$$

where K_{shifted} is the sum of the species-dependent shifted valence and conduction density kernel, which is defined as

$$K_{\text{shifted}} = \sum_L \left(\sigma_{v,L} K_L + \sigma_{c,L}(S_L^{-1} - K_L) \right) \, . \tag{2}$$

The σ_v and σ_c are the shifts for valence and conduction states, respectively, and the sum is over layer L. The scissor shifted eigenvalues are simply

$$H_{\text{shifted}} = H + S K_{\text{shifted}} S \, . \tag{3}$$

The gradient of the scissor energy with respect to the NGWFs can be calculated

using

$$\frac{\partial E_{\text{scissor}}}{\partial \phi_\gamma^*(\mathbf{r})} = K_n^{\beta\alpha} \frac{\partial}{\partial \phi_\gamma^*(\mathbf{r})} \langle \phi_\alpha | \hat{H}_{\text{scissor}} | \phi_\beta \rangle$$

$$= K_n^{\beta\alpha} \frac{\partial}{\partial \phi_\gamma^*(\mathbf{r})} \langle \phi_\alpha | \phi_\eta \rangle K_{\text{shifted}}^{\eta\delta} \langle \phi_\delta | \phi_\beta \rangle \qquad (4)$$

$$= K_{\text{shifted}}^{\beta\delta} S_{\delta\eta} K_n^{\eta\alpha} \left(\phi_\beta + \sum_{ij} \tilde{p}^i(\mathbf{r}) O_{ij} R^j{}_\alpha \right).$$

The approach has been reasonably well tested in the context of LNV calculations. As of April 2019 it has not been validated for EDFT, conduction NGWF optimisation, TDDFT etc, but these would be reasonably expected to work as well.

2   Performing a Species Dependent Scissor Calculation

To activate the shift, the `species_scissor` block must be present. The user must specify (on separate lines) groups of atom types, with each line finishing with two numbers representing the valence and conduction shifts to be applied to that group of species.

For example, for a MoS_2 / $MoSe_2$ heterobilayer, we might use the following to correct the energies of the individual layers:

```
%block species_scissor
Mo1 S  -0.5 0.5
Mo2 Se -0.1 0.8
%endblock species_scissor
```

This would have the effect of opening the gap of the MoS_2 layer by 1eV and opening the gap of the $MoSe_2$ layer by 0.9 eV, and shifting the alignment of the valence bands by 0.4 eV.