# Empirical Pseudopotentials for 3D and 2D Materials: A Unified Approach

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Local empirical pseudopotential (EP) are used to compute the electronic band structure of various semiconductors, and have also been used to study electronic transport [1]. In this method, the potential of each atomic species is described by a pseudopotential $V_{\mathrm{EP}}(\boldsymbol{r})$. Given the EP and the position of each atom, the Schrödinger equation can be solved and the electronic band structure $E_n(\mathbf{k})$ (where $n$ is the band index, and $\mathbf{k}$ is the electron wavevector) can be determined.

Whereas EPs are available for diamond and zinc-blende materials [2], they are specified in terms of form-factors, $V_{\mathrm{EP}}(G)$, at specific reciprocal lattice vectors $\mathbf{G}$. These enable the calculation of the band structure for unstrained bulk materials. However, to calculate the band structure of strained materials, we need the full wavevector dependence of the EPs, $V_{\mathrm{EP}}(q)$, given by smooth functions of the wavevector magnitude $q$. Historically, many different empirical interpolating functions have been used for the construction of these EPs [3-6]. Here we propose a common functional form for the EPs of different materials. We also present an automated method that optimizes the parameters of the EPs to accurately reproduce the bulk band structure of various 3D and 2D materials.

The functional form in reciprocal space for the EPs we propose is constructed as the sum of cosine waves that vanishes at a specified cut-off wavevector $q_{\mathrm{cut}}$:

$$V_{\mathrm{EP}}(q) = \frac{1}{2(N-1)}\left[a[1] + a[N]\cos\left(\frac{\pi(N-1)q}{q_{\mathrm{cut}}}\right) + 2\sum_{n=2}^{N-1} a[n]\cos\left(\frac{\pi(n-1)q}{q_{\mathrm{cut}}}\right)\right]\Theta(q_{\mathrm{cut}} - q) \quad (1)$$

The coefficients $a[n]$ are determined by the discrete cosine transform of the EP parameters $V[q_i]$, with $N$ wavenumbers, $q_i$ equally spaced from 0 to $q_{\mathrm{cut}}$. $V[q_N]$ is fixed at 0 and the other $V[q_i]$ are varied until an optimized solution is found. In Eq. 1, $\Theta(q)$ is the Heaviside step function so that $V(q) = 0$ for $q > q_{\mathrm{cut}}$. Using this definition, $V(q)$ represents a cosine-based interpolation of the parameters $V[q_i]$ within $q_{\mathrm{cut}}$.

These pseudopotential parameters are optimized to match a reference band-structure which we generate from first principles [7] using hybrid functionals [8] in our study. Optimum values of $a[n]$ for a given material are determined using the Broyden–Fletcher–Goldfarb–Shanno algorithm, a quasi-Newton based optimization algorithm [9]. During this optimization, the EP with trial parameters is used for the calculation of the electronic band structure ($E_i$) using the procedure described in Ref. 1. The difference between the calculated band structure and the reference band structure is quantified by an objective function ($d_{\mathrm{obj}}$) defined as:

$$d_{\mathrm{obj}} = \sqrt{\frac{\Sigma_i w_i(E_i^2 - E_{\mathrm{ref}}^2)}{\Sigma_i w_i}}$$

where $i$ runs over all bands and a selected number of $\mathbf{k}$ points, and $w_i$ represent weights that are chosen such that the band structure is primarily matched in the region of interest, i.e. close to the bandgap for electronic transport purposes. The trial parameters are optimized until a minimum value of $d_{\mathrm{obj}}$ is obtained. In Figs.1-4, we show the EP and the band structures corresponding to the optimized set of parameters for bulk Si and phosphorene (monolayer black phosphorus). These calculated band structures reproduce the respective reference band structures very well yielding $d_{\mathrm{obj}} \approx 10$ meV. We are thus able to establish an automated, unified workflow for the EP construction of both three- and two-dimensional materials.

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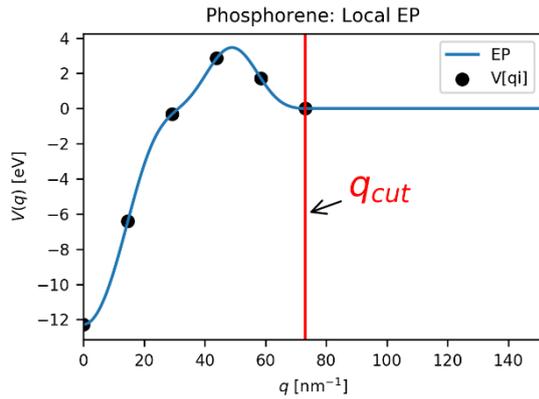
Fig.1: *Local empirical pseudopotential (EP) for phosphorene in reciprocal space. This EP is optimized for a 15 Ry energy cutoff. The black dots represent the optimized EP parameters $V[q_i]$ and $q_{cut}$ represents the reciprocal lattice vector cut-off calculated from the energy cutoff.*
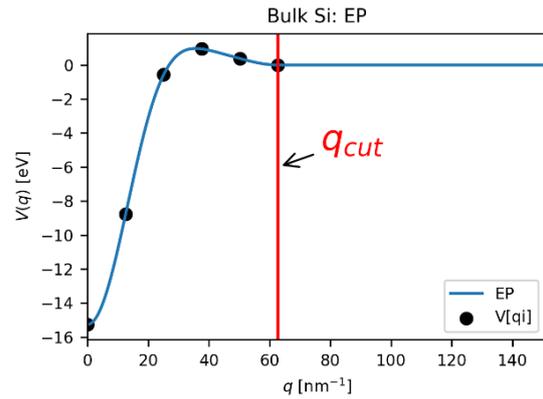


Fig.2: *Local Empirical Pseudopotential (EP) for bulk Si in reciprocal space. This EP is optimized for 11 Ry energy cutoff. The black dots represent the optimized EP parameters $V[q_i]$ and $q_{cut}$ represents the reciprocal lattice vector cut-off calculated from the energy cutoff.*
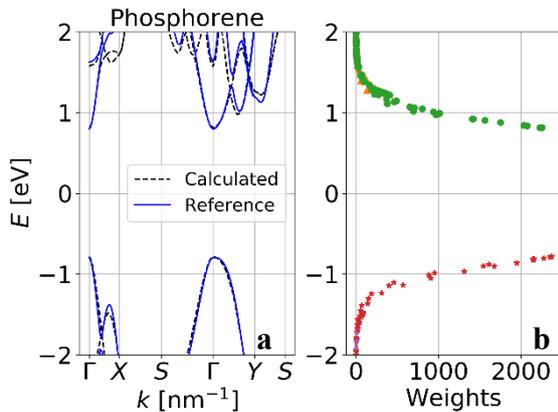


Fig.3: **a**: *Electronic band structure for phosphorene calculated at 120 k-points. The blue curve represents the reference band structure obtained from first principles and the dashed black curve represents the band structure calculated using EP given by Eq. 1.* **b**: *Weight distribution used for finding the optimized EP.*
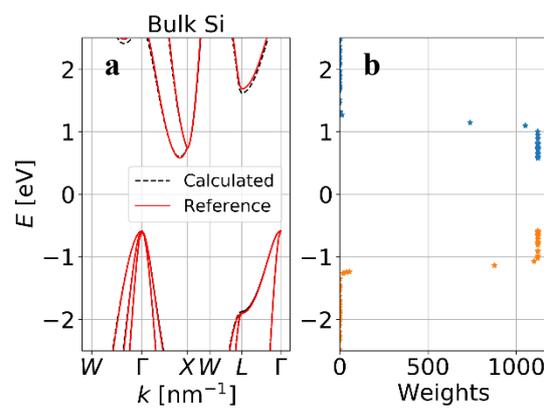


Fig.4: **a**: *Electronic band structure for bulk Si calculated at 100 k-points. Red curve represents the reference band structure obtained from first principles and the dashed black curve represents the band structure calculated using the EP given by Eq. 1.* **b**: *Weight distribution used for finding the optimized EP.*