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Silicene band structure calculations using a semi-empirical pseudopotential method with spin and spin-orbital coupling included

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Abstract. A new approach is proposed for calculating the electronic band structure of silicene in terms of the density functional theory using a model pseudopotential with a small number of adjustable parameters. The approach is based on the self-consistent solution of the Kohn-Sham equation, in which the true potential created by nuclei and all electrons is replaced by an effective potential acting on valence electrons only. As an initial approximation for this potential, it is proposed to use the pseudopotential of bulk silicon, which best determines its band structure. The dispersion of electrons in the most symmetrical directions of the Brillouin zone of silicene has been calculated. It is shown that the band structure of this material determined in the framework of this approach is in qualitative agreement with the results obtained using first-principle methods, as well as the tight-binding method and \( k \cdot p \) perturbation theory.

1. Introduction
Silicene is a 2D allotrope of silicon and, similarly to graphene, it shows a hexagonal honeycomb structure. The atoms of two sublattices in this material are located in different planes displaced parallel to each other by a distance \( \Delta Z \approx 0.44 \) (figure 1) [1]. An interesting feature of the silicene band structure is the presence of valence and conduction bands with linear dispersion crossing at the K and K' points in the Brillouin zone (so-called Dirac cones) in the case when calculations ignore spin-orbit coupling [1]. However, when taking into account the latter effect it is shown that silicene opens a small gap. The material is of interest because it has potential compatibility with existing silicon technologies.

The first band structure calculations of silicene were performed using ab-initio approaches [2, 3]. However, semi-empirical methods such as the tight-binding model [4–6] or the \( k \cdot p \) perturbation theory [7, 8] are always more appreciated, since they allow the calculation results to be fitted to the available experimental data.

In this paper, we use a semi-empirical pseudopotential method. The main idea is to replace the Coulomb potential due to the nuclei and electrons localized on them with a weaker effective potential acting only on the valence electrons of silicon. A model potential for self-consistent calculations in the framework of the density functional theory is proposed as such a potential. It contains empirical parameters that can be varied to ensure that the calculation results are consistent with experimental data.
ΔZ

Figure 1. Crystal structure of silicene. Here ΔZ = 0.44 [1] is the shift between two planes of silicon atoms and \( a = 3.82 \text{ Å} \) [1] is the silicene lattice constant.

2. Kohn-Sham equations
The main step is to solve the single-particle Kohn-Sham equation, which can be represented in Rydberg atomic units as follows [9]:

\[
\left( -\nabla^2 + v_{\text{eff}}(\mathbf{r}) - \varepsilon_i \right) \varphi_i(\mathbf{r}) = 0
\]

(1)

Here \( \varphi_i(\mathbf{r}) \) and \( \varepsilon_i \) are the single particle wave function and electron energy, respectively, \( \mathbf{r} \) is the radius-vector of an electron, and \( v_{\text{eff}}(\mathbf{r}) \) is the effective crystalline potential determined by the expression:

\[
v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \frac{2}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') d\mathbf{r}' + v_{\text{xc}}(\mathbf{r}),
\]

(2)

where \( v(\mathbf{r}) \) is the periodic potential created by individual atoms of the crystal lattice:

\[
v(\mathbf{r}) = \sum_\alpha \sum_n V(\mathbf{r} - \mathbf{\tau}_\alpha - \mathbf{a}_n).
\]

Here \( \mathbf{a}_n \) are the Bravais lattice vectors, \( \mathbf{\tau}_\alpha \) are the basis vectors, and \( V(\mathbf{r}) \) is the spherically symmetric local potential. The second term on the right side of equation (2) is the Hartree term, and \( v_{\text{xc}}(\mathbf{r}) \) is the exchange and correlation potential, which is calculated using the \( X_\alpha \) approximation [10]:

\[
v_{\text{xc}}(\mathbf{r}) = \alpha \left( n(\mathbf{r}) \right)^{\frac{1}{3}}.
\]

(3)

where \( \alpha \) is chosen to reach an agreement with the Wigner interpolation formula at the average valence electron density of Si.

The Hartree term and exchange-correlation potential are functionals of the electron density:

\[
n(\mathbf{r}) = \sum_i^N |\varphi_i(\mathbf{r})|^2.
\]

(3)

In this expression, the sum goes over all occupied states. Since the effective potential (2) depends on the electron density \( n(\mathbf{r}) \) (3) determined by the wave functions, the Kohn-Sham equation (1) is non-linear and must be solved self-consistently. We use a plane-wave basis set, since the pseudopotential makes it more effective.

3. Bravais lattice
Silicene possesses translational symmetry only in two directions of \( x \) and \( y \). However, when solving a problem in a plane-wave basis, it is convenient to consider an artificial structure with translational symmetry in all three directions. In this case, the lattice period along the third direction of \( z \) is chosen sufficiently large in order to eliminate the effects of electron tunneling into adjacent layers. Since the
lattice parameter of silicene $a$ is chosen as the unit of length, the primitive vectors of its Bravais lattice can be represented as:

$$a_1 = \left( \frac{1}{2}, \frac{\sqrt{3}}{2}, 0 \right), a_2 = (1, 0, 0), a_3 = \left( 0, 0, \frac{D}{a} \right).$$

Here $D$ is the distance between the layers. In our calculation, we took $D = 10 \text{ Å}$.

The process of calculating the electron density $n(r)$ involves integrating the periodic function of a wave vector $k$ over the entire Brillouin zone. To optimize the calculations, the integration was replaced by the summation over the finite grid of carefully selected points. These points were chosen according to the Monkhorst and Pack method [11]:

$$k_{p,r,s} = \mu_p b_1 + u_r b_2 + u_s b_3,$$

$$u_r = \frac{2r - q_i - 1}{2q_i}, r = 1, 2, ..., q_i,$$

where $b_i$ is the reciprocal lattice vectors, and $q_i$ is the number of points in the direction of $b_i$. According to the symmetry, the number of necessary points can be reduced by determining weighting factors $\omega_i$ that take into account their multiplicity. In this case, the final expressions for the electron density $n(r)$ and its Fourier transform $n(b)$ take, respectively, the form:

$$n(r) = \sum_{\mu, i} \omega_i |\varphi_{i, \mu}(r)|^2,$$

$$n(b) = \sum_{\mu, i} \sum_{b'} \omega_i \varphi_{i, \mu}(b - b') \varphi_{i, \mu}(b').$$

Here $\mu$ numbers the zones filled with valence electrons.

4. Model potential

In the plane-wave basis set, the Hamiltonian of the electron from equation (1) can be rewritten as follows:

$$H_{bb'}(k, k') = \left[ (b + k)^2 \delta_{bb'} + v_{\text{eff}}(b - b') \right] \delta_{kk'} = H_{bb'}(k) \delta_{kk'},$$

where $v_{\text{eff}}(b - b')$ is the Fourier transform of the effective crystalline potential $v_{\text{eff}}(r)$:

$$v_{\text{eff}}(b - b') = \frac{1}{\Omega} \int v_{\text{eff}}(r)e^{-i(b - b')r} dr.$$

Here $\Omega$ is the volume of the unit cell. According to expression (2), $v_{\text{eff}}(r)$ can be represented as the sum of three terms:

$$v_{\text{eff}}(b - b') = v(b - b') + v_H(b - b') + v_{xc}(b - b').$$

Taking into account the spherical symmetry of the local potential $V(r)$, it can be shown that:

$$V(b) = \frac{1}{\Omega} \int v(r)e^{-ibr} dr = V(b)\cos(\tau),$$

where $\tau_1 = \tau$ and $\tau_2 = \tau$. A model function was chosen as the Fourier transform $V(b)$ of the local potential:

$$V(b) = -\frac{8\pi Z_v}{\Omega b^2} \exp \left( -\frac{b^2}{X_1} \right) + X_2 \exp \left( -\frac{(|b| - X_3)^2}{X_4} \right) + X_5.$$
The constants $\chi_i$ in these formulas are adjustable parameters. Their values were selected to fit experimental energy gaps in bulk silicon. Thus, we made an attempt to predict the properties of the material, but with the empirical data on silicene available, the parameters can be redefined to be more accurate. In this work, $\chi_1 = 4.318$, $\chi_2 = 23.829$, $\chi_3 = 1.432$, $\chi_4 = 1.503$, $\chi_5 = 1.134$.

We can deduce from expression (5) that the first term diverges when $b^2 = 0$. However, it is compensated by the corresponding Fourier transform of the Hartree term

$$v_H(b) = 8\pi n(b) \frac{b^2}{2}.$$ 

Here, it is taken into account that

$$n(0) = \frac{Z}{\Omega}.$$ 

Indeed, taking the limit, we have:

$$\lim_{b^2 \to 0} (v_H(b) + V(b)) = \chi_2 \exp\left(-\frac{\chi_3}{\chi_4}\right) + \chi_5.$$ 

The Fourier transform of the exchange and correlation term $v_{xc}(r)$ is determined numerically. A finite basis set can be obtained by truncating the terms in expansion up to some cutoff on the kinetic energy of the plane wave.

$$\left(\frac{a}{2\pi}\right)^2 (b+k)^2 \leq 24.$$ 

As a result, the solution of the problem at each iteration step is reduced to the calculation of the eigenvalues and eigenvectors of the corresponding Hamiltonian matrix (4). At the end of each step, the screening potential is recalculated using the CDIIS algorithm [12]. The process is repeated until convergence is achieved.

After the self-consistent potential $v_{eff}^{SCF}(b)$ is obtained at the last iteration, the spin and spin-orbit coupling can be included by introducing the correction to the Hamiltonian (4), which can be represented in the plane-wave basis as follows:

$$H_{bs,b's'}^{SO}(k,k') = A \cdot \sigma_{ss'} \cdot \left[i \cdot (b - b') \times (b - k')\right] \cdot v_{eff}^{SCF}(b - b') \cdot \delta_{kk'} = H_{bs,b's'}^{SO}(k) \delta_{kk'},$$

Here $\sigma$ is the Pauli matrices, and $A$ is the adjustable parameter.

Finally, the expression for the silicene Hamiltonian with spin and spin-orbit interaction included takes the form:

$$H_{bs,b's'}(k) = H_{bb'}(k) \delta_{ss'} + H_{bs,b's'}^{SO}(k).$$

5. Results

Taking into account all of the above, the band structure of silicene in the $\Gamma$MK$\Gamma$ directions of the Brillouin zone was obtained using six adjustable parameters. The calculations that exclude spin-orbit coupling (figure 2) are in good agreement with the results of calculations from the first principles [3, 4], as well as using the tight-binding model [5, 6] and the $k \cdot p$ perturbation theory [7, 8]. In particular, Dirac cones are present at the K and K’ points of the Brillouin zone. Indeed, as expected, a small band gap of 4 meV has appeared when taking into account the spin in silicon (figure 3). The dispersion when moving away from the K and K’ points is linear. In general, it corresponds to the data from [1].
6. Summary
We presented the semi-empirical pseudopotential for Si that best fits the available experimental data on bulk silicon. It was applied to calculate the band structure of silicene in the most symmetrical directions of the Brillouin zone. The data obtained are in good agreement with previous first-principle and semi-empirical calculations. Thus, we made an attempt to predict the properties of freestanding silicene. However, if empirical data on the material itself are available, the model potential could be redefined to fit it.

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