An efficient k · p method for the calculation of total energy and electronic density of states

Marcella Iannuzzi and Michele Parrinello
CSCS - Swiss Center for Scientific Computing, via Cantonale, CH-6928 Manno
and
Physical Chemistry ETH, Hönggerberg HCI, CH-8093 Zurich, Switzerland.

An efficient method for calculating the electronic structure in large systems with a fully converged BZ sampling is presented. The method is based on a k · p—like approximation developed in the framework of the density functional perturbation theory. The reliability and efficiency of the method are demonstrated in test calculations on Ar and Si supercells.

In periodic systems the correct description of electronic structure requires an exhaustive sampling of the Brillouin Zone (BZ). However for large systems, such as those that are employed in ab-initio molecular dynamics, this can be too expensive and very often the sampling is limited to the Γ point of the BZ. This is quantitatively accurate for very large systems and/or wide gap insulators. In all the other cases a correct sampling of the BZ is to be recommended. Another limitation of Γ calculations is the very coarse description that they give of the electronic density of states, even for rather large supercells.

However, since full BZ sampling can be too costly, k · p—like approaches have been suggested by several authors in order to include k ≠ 0 states at reduced computational costs. In these works it has been suggested that the calculation of the k dispersion of eigenvalues can be conducted in a restricted Hilbert space. Robertson and Payne have proposed that this Hilbert space could be constructed from the occupied and a limited number of unoccupied eigenfunctions of the Γ only KS Hamiltonian. Since by increasing the number of unoccupied states one converges to the exact result, this method is in principle exact. Unfortunately, the number of excited states that needs to be included in order to achieve a satisfactory convergence is large, therefore this approach has had limited impact. Kohanoff and Scandolo have proposed a procedure in which the basis vectors of the Hilbert space are variationally improved, along with the electronic wavefunction coefficients. Still, in the non-local PP formalism, this procedure would become rather expensive and actually it has been applied only to the local PP, which is quite restrictive.

Here we adapt a recently developed version of density functional perturbation theory (DFPT) to calculate the finite k corrections. We show that this can give very accurate energies for systems of a few hundred atoms for a semiconductor like Si, and even smaller for an insulator like Ar, producing a significant improvement of the Γ only sampling at reduced computational cost. Furthermore we show that for large systems, the Hilbert space of the occupied eigenstates supplemented by the perturbative corrections provide a excellent description of the electronic density of states (DOS) at a much reduced computational cost.

We shall restrict ourselves to the case of a semiconductor or insulator, where all states ψkm(r) labeled by the state index m and by the BZ vector k are doubly occupied. We shall develop our method within the context of pseudopotential (PP) formalism, but it can easily be extended to other electronic structure schemes. In order to be definite we shall consider fully non-local PP of the Kleinman-Beylander type composed of a local part, \( V_{loc}(r) \), and a non-local part, \( \sum_{L} |P_{I,L}\rangle \omega_{L} \langle P_{I,L}| \), where the sum runs over all nuclei I and the angular momentum channels L. The Bloch theorem allows us to write \( ψ_{km}(r) = u_{km}(r)e^{i\mathbf{k} \cdot \mathbf{r}} \) where \( u_{km}(r) \) has the lattice periodicity. In terms of the \( u_{km} \) the Kohn and Sham (KS) density functional can be rewritten as

\[
E_{KS} = \sum_{BZ} E(k) \tag{1}
\]

where the contribution from each k vector reads

\[
E(k) = 2 \sum_{m}^{occ} \left\{ |u_{km}|^2 - \frac{1}{2} \nabla^2 |u_{km}| + \frac{1}{2} \mathbf{k}^2 \right. \\
+ \left. \langle u_{km} | i\mathbf{k} \cdot \nabla | u_{km} \rangle \right. \\
+ \left. \sum_{L} \left[ \langle u_{km} \exp(i\mathbf{k} \cdot \mathbf{r}) | P_{I,L} \rangle \omega_{L} \right. \\
\left. - \langle P_{I,L} | u_{km} \exp(i\mathbf{k} \cdot \mathbf{r}) \rangle \right] \right\} \\
+ \int \rho(r) V_{loc}(r) dr + E_{Hxc}(\rho(r)) \tag{2}
\]

The sum in m is over the occupied states. The electronic charge density is given by

\[
\rho(r) = 2 \sum_{m}^{occ} |u_{km}(r)|^2 \tag{3}
\]

\( E_{Hxc} \) is the sum of the Hartree and exchange and correlation contributions to the energy density functional. In the definition of the energy functional the orthonormality
the results of a $\Gamma$ only calculation, and the $u^{(0)}$ where the field, $u^{(1)}$'s are the 0th order wavefunctions, namely the first order corrections. Since in the absence of a magnetic field, $u^{(0)}$'s and $u^{(1)}$'s can be made real the first order correction to the density vanishes identically.  

To the second order in $k$, $E(k)$ becomes:

$$E(k) = E_{KS}(\Gamma) + \frac{1}{2}k^2 + \sum_{\alpha\beta} k_{\alpha} k_{\beta} \left[ \sum_{I,L} \left( \langle u^{(0)}_{\alpha} | r_{\alpha} | P_{I,L} \rangle \omega_{L} \langle P_{I,L} | r_{\beta} | u^{(0)}_{\beta} \rangle - \frac{1}{2} \langle u^{(0)}_{\alpha} | r_{\alpha} r_{\beta} | P_{I,L} \rangle \omega_{L} \langle P_{I,L} | u^{(0)}_{\beta} \rangle - \frac{1}{2} \langle u^{(0)}_{\alpha} | P_{I,L} \omega_{L} | (P_{I,L} | r_{\alpha} r_{\beta} | u^{(0)}_{\beta} \rangle \right) + \sum_{\alpha\beta} \left( \langle iu^{(1)}_{\alpha \beta} | - i \nabla_{\beta} | u^{(0)}_{\alpha} \rangle + \langle u^{(0)}_{\alpha} | - i \nabla_{\beta} | u^{(1)}_{\alpha \beta} \rangle + \sum_{I,L} \left( \langle iu^{(1)}_{\alpha \beta} | - i r_{\beta} | P_{I,L} \rangle \omega_{L} \langle P_{I,L} | u^{(0)}_{\alpha} \rangle + \langle u^{(0)}_{\alpha} | - i r_{\beta} | P_{I,L} \rangle \omega_{L} \langle P_{I,L} | iu^{(1)}_{\alpha \beta} \rangle + \langle u^{(0)}_{\alpha} | P_{I,L} \omega_{L} | P_{I,L} | - i r_{\beta} | u^{(1)}_{\alpha \beta} \rangle + \langle u^{(1)}_{\alpha \beta} | H^{0}_{KS} | u^{(0)}_{\alpha} \rangle - \frac{1}{2} \omega_{m}^{0} | u^{(1)}_{\beta m} \rangle \right) \right. \right] \right] (6)

Once the $u^{(0)}$'s are calculated, the $u^{(1)}$'s can be determined by minimizing the second order correction of the functional, $E^{(2)}$, relative to the $u^{(1)}$'s. The minimization procedure is to be supplemented by the restricted orthonormality condition

$$\langle u^{(0)}_{m} | u^{(1)}_{n} \rangle = 0 \ \forall \ m, n \ and \ \alpha \ (7)$$

It can be seen that $E^{(2)}$ has the same structure as the standard form of the variational DFPT \[1\]. The only peculiarity is that the quadratic terms describing the effect of the change in $\rho$ due to the perturbation are absent. Such a simplification is a consequence of the nature of the perturbation and occurs also, for instance, in the case of the calculation of NMR chemical shifts \[1\]. In the DFPT the terms that are linear in $\{u^{(1)}_{\alpha \beta} \}$ express the perturbative coupling \[1\]. In our case for a purely local PP the perturbation appears as a coupling to the current operator $-i \nabla$, as is to be expected from a $k \cdot p$ scheme. Since it is well known that a non-local PP also affects the current operator, it is not surprising that in the non-local case some extra perturbation terms appear. We note that as written in Eq.(6), the $k$ expansion has only a formal character, since the position operator, in the non-local PP terms, is ill defined in a periodic system. If however we express the full non-local PP projectors in the reciprocal space and then expand in $k$ the non-local energy terms, we arrive at well-defined expressions that can be straightforwardly calculated \[2\]. In practice we first perform a $\Gamma$ only calculation and then, using the variational DFPT module developed in our group \[3\], we perform three separate variational calculations to determine $\{u^{(1)}_{m}, u^{(1)}_{m}, u^{(1)}_{m} \}$. The calculations of $\{u^{(0)}_{m} \}$ and $\{u^{(1)}_{m} \}$ can take full advantage of the fact that these quantities are real. Once the $\{u^{(1)}_{m} \}$ are known, $\Delta_{\alpha \beta} = \delta^{2}E/\delta k_{\alpha} \delta k_{\beta} |_{k=0}$ can be evaluated and summing over the BZ we arrive at the following energy estimate

$$E = E_{\Gamma} + \frac{1}{2} \sum_{BZ} \sum_{\alpha \beta} k_{\alpha} k_{\beta} \Delta_{\alpha \beta} \ (8)$$

Therefore, the computational effort required by the whole procedure is comparable to the optimization of four independent sets of wavefunctions \[1\] and it does not depend on the number of $k$-points used in the BZ sampling.

We tested the efficiency of the method on the crystalline systems of Ar and Si. For these two systems we have considered supercells of increasing size and compared the $\Gamma$ only calculation with and without the perturbation theory correction to the exact result obtained performing a full BZ sampling in the primitive cell.

The Ar fcc unit cell, with 9.94 a.u. lattice constant, contains one atom and 8 valence electrons. We describe this system by means of a Goedecker PP \[10\] and the LDA functional. The converged total energy is achieved by the standard CPMD \[11\] wavefunction optimization, over a $8 \times 8 \times 8$ Monkhorst-Pack (MP) \[12\] mesh in the BZ of the primitive cell. Calculating the total energy with the $\Gamma$ point only produces errors which decreases with the system size, as shown in Fig. 6. As expected in this case, since Ar bands are rather flat, the $k \cdot p$ approach converges very rapidly with the system size.

We turn now to the study of the prototypical semiconductor, Si. The Si unit cell contains 2 atoms and 8 valence electrons. In this case we use the Troullier-Martins norm-conserving PP \[13\] and the Ceperley-Alder local density approximation to the exchange-correlation term \[14\]. Convergence of total energy for this unit cell is achieved by an integration over the $(15 \times 15 \times 15)$ MP mesh. As shown in Fig. 2, the DFPT correction produces an important improvement, such that the total energy er-
and the contribution of the individual states cannot be obtained if for any \( \mathbf{k} \) one diagonalizes the \( \mathbf{k} \) dependent KS Hamiltonian

\[
H(\mathbf{k}) = H(0) + \frac{1}{2} \mathbf{k}^2 - i \mathbf{k} \cdot \nabla \\
+ \sum_{I,L} e^{-i \mathbf{k} \cdot \mathbf{r}} |P_{IL}| \omega_L \langle P_{IL} | e^{i \mathbf{k} \cdot \mathbf{r}} \\
- \sum_{I,L} |P_{IL}| \omega_L \langle P_{IL} |
\]  

in the Hilbert space spanned by the vectors \( \{u_m^0\} \) and \( \{\tilde{u}_m^{(1)}\} \), which has dimension \( 2N \), where

\[
\tilde{u}_m^{(1)} = i k_x u_{m}^{(1)} + i k_y u_{m}^{(1)} + i k_z u_{m}^{(1)}.
\]

These vectors are orthogonal to the subspace \( \{u_m^0\} \) but they are not mutually orthogonal. We perform the orthonormalization by means of the Löwdin method, which requires the overlap matrix

\[
S_{m,n}(\mathbf{k}) = \langle \tilde{u}_{km}^{(1)} | \tilde{u}_{kn}^{(1)} \rangle = \sum_{\alpha \beta} k_\alpha k_\beta \langle u_{km}^0 | u_{kn}^0 \rangle
\]

to be calculated for each \( \mathbf{k} \) vector. The matrices \( \langle u_{km}^0 | u_{kn}^0 \rangle \) can be calculated only once and then stored for later use. Similarly it can easily be shown that most of the matrix elements of \( H(\mathbf{k}) \) can be expressed in terms of \( \mathbf{k} \) independent matrices, which can be calculated outside the \( \mathbf{k} \) loop. The only exception is the non-local PP term, which requires the evaluation of the projectors \( \langle P_{IL} | e^{i \mathbf{k} \cdot \mathbf{r}} u_m^0 \rangle \) and \( \langle P_{IL} | e^{i \mathbf{k} \cdot \mathbf{r}} u_{n}^{(1)} \rangle \). However, fully in the spirit of our method, we can expand these projectors to second order in \( \mathbf{k} \), which reduces the evaluation to a linear combination of \( \mathbf{k} \) independent quantities.

We have tested our method on Ar and Si. Once again, for Ar the convergence is very fast and already for the 32-atom supercell, the \( \mathbf{k} \cdot \mathbf{p} \) approach gives results that are practically indistinguishable from the real ones. We illustrate here the more interesting case of Si. In Fig. 3(a) we report the \( \Gamma \) point only DOS, as resulted for a 128-atom Si supercell. It is easily seen that this is a caricature of the real DOS. For the same system a much better description can be obtained using a \((4 \times 4 \times 4)\) MP mesh, as shown in Fig. 3(b). In the same picture we demonstrate that our method gives accurate results and that the use of the expansion in the evaluation of the non-local PP introduces only small errors. While the result of the full calculation and of the \( \mathbf{k} \cdot \mathbf{p} \) method are comparable, the latter is computationally more efficient by at least two orders of magnitude. This allows us to calculate easily the electronic DOS for the 128-atom supercell including 4096 \( \mathbf{k} \) points on an Intel Xeon PC. The result is compared in Fig. 3 with the DOS obtained by a standard method on
FIG. 3: Electronic density of state calculated for the Si supercell containing 128 atoms. a) \( \Gamma \) only DOS, b) Comparison between the standard CPMD (dashed) and the DFPT (solid) results, by using a \((4 \times 4 \times 4)\) MP mesh.

the primitive cell of two atoms and with 8000 equally distributed \(k\) points. The only symmetry used is inversion. For both calculations the tetrahedron method \([15]\) was used in order to perform the \(k\) point integration in the BZ. The very good agreement between the two curves demonstrates the usefulness of our approach.

In conclusion, we have shown that even for systems that are by present computational standards modest in size, the \( \mathbf{k} \cdot \mathbf{p} \) method implemented here is accurate and computationally efficient. It is therefore now possible to perform efficient \textit{ab-initio} molecular dynamics calculations with fully converged BZ sampling.

We are very grateful to the Max Planck Institut für Festkörperforschung, (Stuttgart, Germany) for its support during the initial phases of this research.

[1] I.J. Robertson and M.C. Payne, \textit{J. Phys. Condens. Matter} \textbf{2}, 9837 (1990).
[2] S. Scandolo and J. Kohanoff, \textit{Phys. Rev. B} \textbf{62}, 15499 (2000).
[3] S. Baroni, P. Giannozzi and A. Testa, \textit{Phys. Rev. Lett.} \textbf{58}, 1861 (1987).
[4] X. Gonze \textit{Phys. Rev. A}, \textbf{52}, 1096 (1995); X. Gonze and J.P. Vigneron, \textit{Phys. Rev. B} \textbf{39}, 13120 (1989)
[5] A. Putrino, D. Sebastiani and M. Parrinello, \textit{J. Chem. Phys.} \textbf{113}, 7102 (2000).
[6] L. Kleinman and D.M. Bylander, \textit{Phys. Rev. Lett} \textbf{48}, 1425 (1982).
[7] N.W. Ashcroft and N.D. Mermin, \textit{Solid State Physics}, (Tokyo: Holt Saunders) (1976).
[8] W. Kohn and L.J. Sham, \textit{Phys. Rev.} \textbf{140}, A1133 (1965).
[9] M. Iannuzzi and M. Parrinello, to be published.
[10] S. Goedecker, M. Teter and J. Hutter, \textit{Phys. Rev B} \textbf{54}, 1703 (1996).
[11] J. Hutter et al. CPMD MPI für Festkörperforschung and IBM Zurich Research Laboratory (1995-1999)
[12] H.J. Monkhorst and J.D. Pack, \textit{Phys. Rev B} \textbf{13}, 5188 (1973).
[13] N. Troullier and J.L. Martins, \textit{Phys. Rev. B} \textbf{43}, 1993 (1991).
[14] D.M. Ceperley and B.J. Alder, \textit{Phys. Rev. Lett.} \textbf{45}, 566 (1980).
[15] M. Hanke, W. Kuhn and R. Strehlow, \textit{Physica Status Solidi B - Basic Research} \textbf{123}(1), k39-k42 (1984).