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# Fock-Exchange for periodic structures in the real-space formalism and the KLI approximation

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The calculation of Fock-exchange interaction is an important task in the computation of molecules and solids properties. In this work we describe how we implement in the real-space formalism the Fock Exchange with the KLI approximation for the OEP equation for 3D periodic systems. The implementation is demonstrated within the PARSEC real-space pseudopotential code that uses a discrete uniform grid and norm conserving pseudopotentials for the ionic potentials.

## 1 Introduction

In recent years there is an increasing interest in approaches that combine Density Functional Theory (DFT)<sup>1</sup> and Fock-exchange, to create methods with higher reliability in prediction of the electronic structure of materials. Such methods with the general name of Hybrid Functionals, can be implemented either within the Generalized Kohn-Sham method (GKS)<sup>2</sup> where the energy is minimized with respect to the orbitals, or strictly within pure DFT by requiring minimization of the energy with respect to the electronic density. While both methods have advantages and disadvantages, an advantage of the latter is that it leads to a local potential that can be used to solve the Kohn-Sham (KS) equations<sup>3</sup> and also serve as an efficient starting point for more advanced calculations such as GW<sup>4-6</sup>. A disadvantage of this method is that the minimization with respect to energy leads to a complicated integral-differential equation, known as the Optimized Effective Potential (OEP)<sup>7,8</sup>. While there are methods to solve the OEP equation, its general solution is usually computationally intensive. A useful approximation for the OEP solution was suggested by Krieger, Li and Iafrate (KLI)<sup>9</sup> in 1992. In this approximation one of the terms in the OEP equation is neglected and so one can get immediately a local potential without having to solve the full OEP equation. The KLI approximation for orbital dependent functionals can also be used as a good starting point for iterative methods to solve the OEP equation<sup>10</sup>. The implementation of Fock Exchange, also called Exact Exchange, within the OEP scheme and KLI approximation has been shown to be useful for the description of solids<sup>5,6,11-17</sup> and is named in the literature xOEP, OEPx, EXX and EXX-KLI. The solution of the KS differential equations requires a

representation for the wave functions, this can be implemented either through the use of basis functions such as planewaves, gaussians, numerical basis sets or wavelets, or through the real-space method<sup>18-23</sup> that uses a discrete grid to represent the wave functions. The real-space method can be used to solve both isolated system and 1D<sup>24</sup>, 2D and 3D periodic systems<sup>21,25</sup>. In this work, we develop the KLI formalism on a real-space grid with 3D periodic boundary conditions. We first show how one can get immediately the expression for exchange on the Born-von Karman (BvK) super-cell and how to move from the super-cell to using k-point symmetry on the lattice unit cell. We then discuss the exchange singularity and its manifestation in the real-space formalism. The implementation is done within the PARSEC real-space<sup>18-20</sup> code and the results are compared to plane waves calculations.

## 2 Real-Space pseudopotential method in periodic systems

The real space method is based on sampling the orbitals on an equally spaced grid and on converting the KS differential equations into high order finite difference equations. In this section we discuss briefly the 3D periodic implementation details within the PARSEC code. We write first the spin polarized KS equations as:

$$\left(-\frac{\nabla^2}{2} + \hat{V}_{KS}(\vec{r})\right) \varphi_{j\sigma}(\vec{r}) = \varepsilon_{j\sigma} \varphi_{j\sigma}(\vec{r})$$

$$\rho_{\sigma}(\vec{r}) = \sum_{j=1}^{N_{\sigma}} |\varphi_{j\sigma}(\vec{r})|^2$$

$$\rho(\vec{r}) = \rho_{\uparrow}(\vec{r}) + \rho_{\downarrow}(\vec{r}) \quad (1)$$

where  $\rho(\vec{r})$  is the electron density,  $\hat{V}_{KS} = \hat{V}_{ps} + V_H + V_{XC}$

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and  $\hat{V}_{ps}(\vec{r}) = \sum_{a=1}^{N_{atoms}} V_{ps}^a(\vec{r})$  is the pseudopotential ionic potential<sup>18,19</sup>,  $V_H$  is the Hartree scalar electrostatic interaction potential and  $V_{XC}$  is the scalar exchange correlation potential. We use the fornberg<sup>26</sup> formulation of high order finite difference to write:

$$\frac{\partial^2 \phi_{m\sigma}(x_i, y_j, z_k)}{\partial x^2} = \sum_{n=-N}^{n=N} \frac{C_n}{h^2} \phi_{m\sigma}(x_i + nh, y_j, z_k) + \mathcal{O}(h^{2N}) \quad (2)$$

Doing so to all second derivatives, the Laplacian is replaced by a finite difference discrete operator. The resulting finite difference equation is solved as described in<sup>18,19</sup>. To solve the equation in a finite domain we restrict the wave functions  $\phi_{m\sigma}$  to be zero outside the domain and solve the KS equations over that domain. The same method can be used for 3D periodic calculations by applying the Bloch condition,  $\phi_{\vec{k}\sigma}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}\sigma}(\vec{r})$ , where  $u_{\vec{k}\sigma}(\vec{r} + \vec{R}) = u_{\vec{k}\sigma}(\vec{r})$  is a periodic function on the lattice, and writing:

$$\left( -\frac{(\vec{\nabla} + i\vec{k})^2}{2} + V_H + V_{xc} + e^{-i\vec{k}\cdot\vec{r}} \hat{V}_{ps}(\vec{r}) e^{i\vec{k}\cdot\vec{r}} \right) u_{\vec{k}\sigma}(\vec{r}) = \epsilon_{\vec{k}} u_{\vec{k}\sigma}(\vec{r})$$

$$\rho_{\sigma}(\vec{r}) = \sum_{\vec{k}} \sum_{j=1}^{N_{\sigma}(\vec{k})} f_{j\vec{k}\sigma} |u_{j\vec{k}\sigma}(\vec{r})|^2$$

$$\rho(\vec{r}) = \rho_{\uparrow}(\vec{r}) + \rho_{\downarrow}(\vec{r}) \quad (3)$$

where  $f_{j\vec{k}\sigma}$  is the electron occupation of the orbital which for insulators is either 1 or 0. The normalization is over the BvK cell -  $\int_{\Omega} |u_{\vec{k}\sigma}(\vec{r})|^2 dr = N_k \int_V |u_{\vec{k}\sigma}(\vec{r})|^2 dr = 1$ , where  $\Omega$  is the BvK cell volume,  $V$  the unit cell volume, and  $N_k$  the number of k-points\*. The electrostatic term is solved with periodic boundary conditions as described in<sup>25</sup>. It is also possible to make the system periodic in one<sup>24</sup> or two<sup>25</sup> dimensions and not periodic in the other dimensions. An important detail is the treatment of the non-local part of the ionic potential. One typically uses the Kleinman-Bylander method<sup>27</sup> to describe the non local part of the pseudopotential and so write for the ionic potential of a given ion:

$$\hat{V}_{ps}^a \phi_{nk\sigma}(\vec{r}) = V_{loc}^a(r_a) \phi_{nk\sigma}(\vec{r}) + \sum_{l,m} G_{nk\sigma,lm}^a \tilde{u}_{lm}(\vec{r}_a) \Delta V_l(r_a) \quad (4)$$

Where  $\vec{r}_a = \vec{r} - \vec{R}_a$ ,  $r_a = |\vec{r} - \vec{R}_a|$ , and  $\tilde{u}_{lm}(\vec{r}_a)$  is the atomic pseudo wave function corresponding to angular momentum  $lm$  and the projection coefficients are given by:

\* We use this normalization throughout the text. Another common normalization is to set  $\int_V |u_{\vec{k}\sigma}(\vec{r})|^2 dr = 1$ , with such normalization it is required to divide by  $N_k$  the expression for  $\rho$  in Eq.3

$$G_{nk\sigma,lm}^a = \frac{1}{\langle \Delta V_{lm}^a \rangle} \int \tilde{u}_{lm}(\vec{r}_a) \Delta V_l(r_a) \phi_{nk\sigma}(\vec{r}) d^3 r$$

$$= \frac{1}{\langle \Delta V_{lm}^a \rangle} \int \tilde{u}_{lm}(\vec{r}_a) \Delta V_l(r_a) e^{i\vec{k}\cdot\vec{r}} u_{nk\sigma}(\vec{r}) d^3 r \quad (5)$$

with:

$$\langle \Delta V_{lm}^a \rangle = \int \tilde{u}_{lm}(\vec{r}_a) \Delta V_l(r_a) \tilde{u}_{lm}(\vec{r}_a) d^3 r \quad (6)$$

The importance of the Kleinman-Bylander form comes from the fact that outside the pseudopotential core cutoff radius,  $r_c$ , we have  $\Delta V_l(r_a) = 0$ , and  $V_{loc}^a(|\vec{r}_a|) = -Z_{ps}/r_a$ . The integrals 5 and 6 are performed on the sphere defined by  $r_a < r_c$ . To get Eq. 3 for the bloch wave functions we multiplied on the left the KS equations for  $\phi_{nk\sigma}$  by  $e^{-i\vec{k}\cdot\vec{r}}$ , while the exponential terms cancel out for the scalar parts of the potential, they are left for the nonlocal part and we get from Eq. 4 the following expression:

$$e^{-i\vec{k}\cdot\vec{r}} \hat{V}_{ion}^a \phi_{nk\sigma}(\vec{r}) = e^{-i\vec{k}\cdot\vec{r}} \hat{V}_{ion}^a e^{i\vec{k}\cdot\vec{r}} u_{nk\sigma}(\vec{r})$$

$$= V_{loc}^a(r_a) u_{nk\sigma}(\vec{r}) +$$

$$e^{-i\vec{k}\cdot\vec{r}} \sum_{l,m} G_{nk\sigma,lm}^a \tilde{u}_{lm}(\vec{r}_a) \Delta V_l(r_a) \quad (7)$$

In periodic systems the crystal structure can force the grid to be non-orthogonal and so there could be mixed derivatives in the laplacian. In our implementation<sup>25</sup> we use auxiliary directions to have a laplacian expression with only pure  $2^{nd}$  derivatives and so we can use directly Eq. 2 for the finite difference expression.

The group of Stephan Kümmel, in collaboration with Leeor Kronik, has added to the PARSEC code support for orbital dependent functionals with the KLI and OEP S-iteration methods<sup>10,28,29</sup> for isolated systems. The Kümmel's group has also extended this to additional functionals such as generalized SIC-KLI and SIC-OEP<sup>30</sup> and to real-time propagation time dependent DFT (RT-TDDFT)<sup>31,32</sup>. This code, for the isolated systems, is used as a starting point for our periodic KLI implementation.

## 3 KLI implementation in periodic systems

### 3.1 Exact exchange energy in periodic systems

We examine first the expression for the exchange energy for isolated systems. This can be given by the general expression:

$$\begin{aligned}
E_X[\rho] &= \\
& -\frac{1}{2} \sum_{\sigma} \sum_{j,m=1}^{N_{occ}} \int_V d^3 \vec{r}_1 \int_V d^3 \vec{r}_2 \frac{\varphi_{j\sigma}^*(\vec{r}_1) \varphi_{m\sigma}^*(\vec{r}_2) \varphi_{m\sigma}(\vec{r}_1) \varphi_{j\sigma}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \\
& = -\frac{1}{2} \sum_{\sigma} \sum_{j,m=1}^{N_{occ}} \int_V d^3 \vec{r}_1 \varphi_{j\sigma}^*(\vec{r}_1) \varphi_{m\sigma}(\vec{r}_1) V_{mj}(\vec{r}_1) \quad (8)
\end{aligned}$$

Where  $V$  is the finite domain volume and we have defined  $V_{mj}$  by:

$$V_{mj\sigma}(\vec{r}_1) \equiv \int_V d^3 \vec{r}_2 \frac{\varphi_{m\sigma}^*(\vec{r}_2) \varphi_{j\sigma}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \quad (9)$$

A good insight as to what happens to Eq. 8 when moving to periodic boundary condition can be gained by looking at the full crystal cell that is defined by the Born-von Karman (BvK) condition:  $\varphi_n(\vec{r} + \sum_i N_i \vec{a}_i) = \varphi_n(\vec{r})$ . In the BvK cell We calculate exactly the same expression for the exchange energy as in Eq. 8, only now the intergarls are evaluated over the BvK cell and the electrostatic interaction is evaluated over all space:

$$\begin{aligned}
E_X[\rho] &= \\
& -\frac{1}{2} \sum_{\sigma} \sum_{j,m=1}^{N_{occ}} \int_{\Omega} d^3 \vec{r}_1 \int_{\mathcal{R}^3} d^3 \vec{r}_2 \frac{\varphi_{j\sigma}^*(\vec{r}_1) \varphi_{m\sigma}^*(\vec{r}_2) \varphi_{m\sigma}(\vec{r}_1) \varphi_{j\sigma}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \\
& = -\frac{1}{2} \sum_{\sigma} \sum_{j,m=1}^{N_{occ}} \int_{\Omega} d^3 \vec{r}_1 \varphi_{j\sigma}^*(\vec{r}_1) \varphi_{m\sigma}(\vec{r}_1) V_{mj\sigma}(\vec{r}_1) \quad (10)
\end{aligned}$$

One immediate problem that arises is that the electrostatic exchange integral diverges. A naïve way of fixing the divergence is to remove the average of  $\varphi_{m\sigma}^* \varphi_{j\sigma}$  over the BvK cell. This is in fact equivalent to removing the divergent DC ( $G=0$ ) term in plane waves formalisms<sup>33–35</sup>. As discussed in<sup>33,34</sup> the removal of the  $G=0$  term introduces a large error in the exchange energy, an error that converges very slowly to zero with the number of k-points. The error is a constant shift of the energy and so does not affect the details of electronic structure but as it depends on the crystal shape, its correction is critical for finding the correct structure. As pointed out by Spencer and Alavi<sup>36</sup> this divergence or singularity term is a result of calculating exchange energy between identical copies of electrons in different BvK cells. This error can be remedied by adding a correction term with an auxiliary function<sup>33–35</sup> or by imposing a screened exchange where the screening length is of the size of the BvK cell<sup>36</sup>. It is worth noting that if one has a code that does EXX-KLI calculation for isolated systems, it is possible to do the exchange calculation over the BvK cell by simply putting periodic boundary conditions and removing the averages of  $\varphi_{m\sigma}^* \varphi_{j\sigma}$  before solving the periodic Poisson equation. It is much more efficient to use Bloch k-point symmetry,

and solve the system on the smaller lattice unit cell, but such a BvK super-cell calculation can be a very good reference for a k-point implementation.

### 3.2 k-space representation

Using Bloch theorem, we write  $\varphi_{n,\vec{k},\sigma}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n,\vec{k},\sigma}(\vec{r})$  where  $u_{n,\vec{k},\sigma}(\vec{r} + \vec{a}_i) = u_{n,\vec{k},\sigma}(\vec{r})$  is a periodic function over the lattice unit cell. It is relatively easy to show that if one uses an equally spaced grid such as Monkhorst Pack<sup>37</sup>, the Bloch orbitals, defined with such a k-point grid of Size  $N_K = N_{K_x} \times N_{K_y} \times N_{K_z}$ , are also a solution for the BvK cell ( $\Gamma$  point) with same dimensions. We can therefore re-write Eq. 10 with the Bloch orbitals:

$$\begin{aligned}
E_X[\rho] &= \\
& = -\frac{1}{2} \sum_{\sigma} \sum_{\vec{k},\vec{q}} \sum_{j,m=1}^{N_{occ}} \int_{\Omega} d^3 \vec{r}_1 \varphi_{j\vec{k}\sigma}^*(\vec{r}_1) \varphi_{m\vec{q}\sigma}(\vec{r}_1) V_{m\vec{q}j\vec{k}\sigma}(\vec{r}_1) \quad (11)
\end{aligned}$$

Where:

$$\begin{aligned}
V_{m\vec{q}j\vec{k}\sigma}(\vec{r}_1) &= \int_{\mathcal{R}^3} d^3 \vec{r}_2 \frac{\varphi_{m\vec{q}\sigma}^*(\vec{r}_2) \varphi_{j\vec{k}\sigma}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \\
& = \int_{\mathcal{R}^3} d^3 \vec{r}_2 \frac{e^{i(\vec{k}-\vec{q})\cdot\vec{r}_2} u_{m\vec{q}\sigma}^*(\vec{r}_2) u_{j\vec{k}\sigma}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \quad (12)
\end{aligned}$$

The potential,  $V_{m\vec{q}j\vec{k}\sigma}(\vec{r}_1)$ , can be found by solving the periodic Poisson equation, we define  $\rho_{m\vec{q}j\vec{k}\sigma}(\vec{r}) \equiv \varphi_{m\vec{q}\sigma}^*(\vec{r}_2) \varphi_{j\vec{k}\sigma}(\vec{r})$ , next we remove the average of  $\rho_{m\vec{q}j\vec{k}\sigma}(\vec{r})$  over the BvK cell (we use  $\Omega = N_K V$  for its volume):

$$\begin{aligned}
\bar{\rho}_{m\vec{q}j\vec{k}\sigma} &\equiv \frac{1}{\Omega} \int_{\Omega} d\vec{r} \rho_{m\vec{q}j\vec{k}\sigma}(\vec{r}) \\
& = \frac{1}{\Omega} \int_{\Omega} d\vec{r} e^{i(\vec{k}-\vec{q})\cdot\vec{r}} u_{m\vec{q}\sigma}^*(\vec{r}) u_{j\vec{k}\sigma}(\vec{r}) \\
& = \frac{\delta_{\vec{k},\vec{q}} \delta_{m,j}}{V} \int_V d\vec{r} u_{m\vec{q}\sigma}^*(\vec{r}) u_{j\vec{k}\sigma}(\vec{r}) \quad (13)
\end{aligned}$$

Since  $\rho_{m\vec{q}j\vec{k}\sigma}(\vec{r}) - \bar{\rho}_{m\vec{q}j\vec{k}\sigma}$  is periodic over the BvK cell and has zero average by construction, we can solve the Poisson equation over the BvK cell:

$$\nabla^2 V_{m\vec{q}j\vec{k}\sigma}(\vec{r}) = -4\pi \left( \rho_{m\vec{q}j\vec{k}\sigma}(\vec{r}) - \bar{\rho}_{m\vec{q}j\vec{k}\sigma} \right) \quad (14)$$

To solve on the smaller unit cell we define  $\tilde{V}_{m\vec{q}j\vec{k}\sigma}(\vec{r}) = e^{i(\vec{q}-\vec{k})\cdot\vec{r}} V_{m\vec{q}j\vec{k}\sigma}(\vec{r})$  and  $\tilde{\rho}_{m\vec{q}j\vec{k}\sigma}(\vec{r}) = e^{i(\vec{q}-\vec{k})\cdot\vec{r}} \rho_{m\vec{q}j\vec{k}\sigma}(\vec{r})$ , since both  $\tilde{V}$  and  $\tilde{\rho}$  are periodic over the unit cell, we can reshape

Eq. 14 to the following equation, that is solved in the smaller lattice unit cell with periodic boundary conditions:

$$\left(\vec{\nabla} + i(\vec{k} - \vec{q})\right)^2 \tilde{V}_{m\vec{q}j\vec{k}\sigma}(\vec{r}) = -4\pi \left(\tilde{\rho}_{m\vec{q}j\vec{k}\sigma}(\vec{r}) - \bar{\rho}_{m\vec{q}j\vec{k}\sigma}\right) \quad (15)$$

We use the conjugate gradient method to iteratively solve Eq. 15.

### 3.3 KLI implementation

We follow the method and symbols of reference<sup>8</sup> to define the OEP and KLI potential, the only difference is that at some point we add the  $\vec{k}$  index and use the periodic boundary conditions.

The OEP approach minimizes the energy of orbital dependent functionals<sup>38</sup>, such as the EXX, with respect to the spin density:

$$V_{xc\sigma}^{OEP} \equiv \frac{\delta E[\{\varphi_{m\sigma}\}]}{\delta \rho_{\sigma}} \quad (16)$$

While it is easy to write Eq. 16, it is not easy to solve it as the orbitals depend only *implicitly* on the density. After applying the chain rule and several mathematical derivations<sup>8</sup> it is possible to arrive for an integral-differential equation for  $V_{xc\sigma}^{OEP}$ . After neglecting some of the terms, it is possible to write the KLI approximation for the potential. We now follow Grabo et al.<sup>8</sup> but add the  $\vec{k}$  index and write:

$$V_{X\sigma}^{KLI}(\vec{r}) = \frac{1}{\rho_{\sigma}(\vec{r})} \sum_{\vec{k}} \sum_{i=1}^{N_{\sigma}} |\varphi_{i\vec{k}\sigma}(\vec{r})|^2 \times \left( U_{X\vec{i}\vec{k}\sigma}(\vec{r}) + \left( \tilde{V}_{X\vec{i}\vec{k}\sigma}^{KLI} - \bar{U}_{X\vec{i}\vec{k}\sigma} \right) \right) + C.C. \quad (17)$$

Where we have assumed that the system is insulating so there are no partial occupations. And we have defined:

$$U_{X\vec{i}\vec{k}\sigma}(\vec{r}) = \frac{1}{\varphi_{i\vec{k}\sigma}^*(\vec{r})} \frac{\delta E_X[\{\varphi_{j\vec{q}}\}]}{\delta \varphi_{i\vec{k}\sigma}} \\ = -\frac{1}{\varphi_{i\vec{k}\sigma}^*(\vec{r})} \sum_{j\vec{q}} f_{j\vec{q}} \varphi_{j\vec{q}\sigma}^*(\vec{r}) V_{i\vec{k}j\vec{q}\sigma}(\vec{r}) \quad (18)$$

$$\bar{U}_{X\vec{i}\vec{k}\sigma} = \int_{\Omega} d\vec{r} \varphi_{i\vec{k}\sigma}^*(\vec{r}) U_{X\vec{i}\vec{k}\sigma}(\vec{r}) \varphi_{i\vec{k}\sigma}(\vec{r}) \\ = N_k \int_V d\vec{r} \varphi_{i\vec{k}\sigma}^*(\vec{r}) U_{X\vec{i}\vec{k}\sigma}(\vec{r}) \varphi_{i\vec{k}\sigma}(\vec{r}) \quad (19)$$

Where  $f_{j\vec{q}}$  are the occupation that in the insulator state can be 0 or 1. Also, we have used the fact that  $U_{X\vec{i}\vec{k}\sigma}(\vec{r})$  can be shown to be periodic over the lattice unit cell. We also define:

$$\tilde{V}_{X\vec{i}\vec{k}\sigma}^{KLI} = \tilde{V}_{X\vec{i}\vec{k}\sigma}^S \\ + \sum_{\vec{q}} \sum_{j=1}^{N_{\sigma}-1} M_{i\vec{k}j\vec{q}\sigma} \left( \tilde{V}_{Xj\vec{q}\sigma}^{KLI} - \frac{1}{2} \left( \bar{U}_{Xj\vec{q}\sigma} + \bar{U}_{Xj\vec{q}\sigma}^* \right) \right) \quad (20)$$

Where in the last summation we omit the highest occupied orbital. In addition we define:

$$\tilde{V}_{X\vec{i}\vec{k}\sigma}^S = \int_{\Omega} d\vec{r} \frac{|\varphi_{i\vec{k}\sigma}(\vec{r})|^2}{\rho_{\sigma}(\vec{r})} \sum_{\vec{q}} \sum_{j=1}^{N_{\sigma}} |\varphi_{j\vec{q}\sigma}(\vec{r})|^2 \frac{1}{2} \left( U_{Xj\vec{q}\sigma}(\vec{r}) + U_{Xj\vec{q}\sigma}^*(\vec{r}) \right) \quad (21)$$

And:

$$M_{i\vec{k}j\vec{q}\sigma} = \int_{\Omega} d\vec{r} \frac{|\varphi_{i\vec{k}\sigma}(\vec{r})|^2 |\varphi_{j\vec{q}\sigma}(\vec{r})|^2}{\rho_{\sigma}(\vec{r})} \quad (22)$$

The integrand in Eq. 21 and 22 is periodic and so the integration can be carried out on the lattice unit cell instead of the BvK cell by  $\int_{\Omega} \rightarrow N_k \int_V$ .

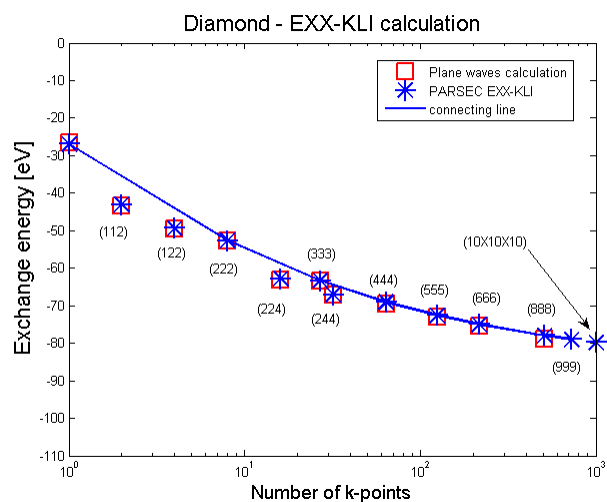
We are now equipped to solve the KLI potential in real-space. The solution of Eq. 15 is done via the conjugate gradient method and the calculation of all integrals is done by a real-space summation over the grid. The solution of Eq. 20 is done by matrix inversion.

## 4 Results

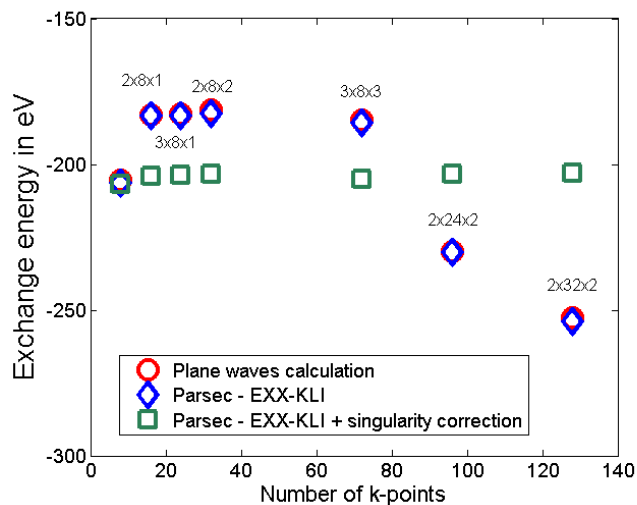
To check our implementation we have compared our results to the plane-waves calculations shown in Carrier et al.<sup>34</sup>. We first checked the behavior of Exchange energy per unit cell,  $E_x/N_k$ , as a function of the k-points grid for the system of carbon diamond with lattice constant of 3.55Å, we have used EXX self consistent norm conserving pseudopotentials<sup>39</sup> and grid spacing of 0.3a.u. The results of those calculations and comparison to plane-waves results are shown in Fig. 1. The slow convergence of the not corrected exchange energy with the number of k-points is evident. In addition to the comparison to plane-waves we have performed also a self consistency check where we checked our k-point implementation of exchange in Eq. 11 against the calculation at  $\Gamma$  point for the appropriate BvK cell as in Eq. 10, this comparison showed an error of less than 1meV.

The next system that we have examined is the trans polyacetylene, described by Carrier et al.<sup>34</sup>. Fig. 2 shows this system with and without their singularity correction. It is evident that the singularity correction leads to a stable result for the exchange energy. of this system.

To further demonstrate our approach we have calculated the band structure of silicon with the implemented EXX-KLI

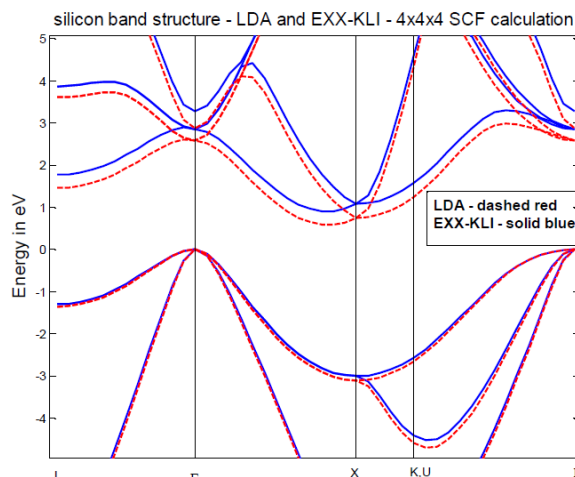


**Fig. 1** EXX energy for carbon diamond structure as a function of k-grid density, comparison is done to plane waves data of Carrier et al.<sup>34</sup>, blue asterisks are PARSEC EXX-KLI calculations, red squares are plane waves results. The quantity shown is the Exchange energy per unit cell -  $E_X/N_k$



**Fig. 2** Polyacetylene EXX-KLI Exchange energy per unit cell,  $E_x/N_k$ , at different k-point grids. Red circles are plane waves calculations by Carrier et al.<sup>34</sup>, blue diamond are the PARSEC EXX-KLI results, squares are the singularity corrected PARSEC results.

method. Here we have used LDA norm conserving pseudopotentials<sup>40</sup> with s/p Cutoff radii of 2.5/2.5. The results are shown in Fig. 3. The band gap from this calculation is  $\sim 0.9\text{eV}$ .



**Fig. 3** Silicon band structure with EXX-KLI implementation. Red dashed line shows LDA results, solid blue line shows EXX-KLI results.

## 5 Summary and outlook

We have shown a real-space implementation of the EXX-KLI approach for periodic systems. We have compared our results to plane-wave calculations and showed that we get similar results for several cases. An important advantage of the implementation is that the memory requirements are linear with the number of k-points or electrons in the system - this is explained further in appendix A. The current implementation is for 3D periodic systems. The real-space formalism allows also calculations of 1D and 2D systems with partial periodicity. The implementation of 1D and 2D would require some modifications in the EXX equations but can follow the approach that was used for the Hartree term in<sup>25</sup>. This can be very interesting for slabs and surfaces as was demonstrated by a recent implementation of EXX for slabs in plane waves formalism<sup>41</sup>. While we have not implemented the OEP iterative scheme<sup>10</sup>, we have included in Appendix B a description of the formalism with k-symmetry. The concept of using first the BvK super-cell can be useful also for the implementation of non-local Hartree-Fock and in fact any orbital dependent functional (e.g. SIC functionals) in periodic systems.

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## 6 Appendix A - Symmetry and memory considerations

The calculation time of exchange depends quadratically on the number of electrons in the system. with  $N_{bands}$  occupied bands and  $N_k$  k-points we would get  $\mathcal{O}(N_{bands}^2 N_k^2)$  calculations. Naively, the memory requirements are also quadratic but we can note that it is enough to keep in memory the  $U_{X\vec{k}}(\vec{r})$  functions and so the memory requirements become reasonable. In addition it is possible to use some of the symmetry properties of  $V_{m\vec{q}j\vec{k}\sigma}(\vec{r}_1)$  to reduce calculation time. First - we note that from the definition of the potential we get:

$$V_{m\vec{q}j\vec{k}\sigma}(\vec{r}) = V_{jkm\vec{q}\sigma}^*(\vec{r}) \quad (23)$$

In addition, it is possible to show, that if inversion symmetry exists, we would get:

$$U_{xi-k\sigma}(\vec{r}) = U_{xik\sigma}^*(\vec{r}) \quad (24)$$

Combining the two properties, the amount of calculations is reduced by a factor of 4. It is possible to use a more general symmetry and reduce the summation to the irreducible Brillouin zone but we did not implement that.

## 7 Appendix B - Equations for full OEP in the periodic case

Finally, although we did not implement the full OEP, it is possible to write also the equation for the full OEP case in the S-iteration<sup>10</sup> method. For completeness we give below the formulation for the periodic case. Following equation 5 in<sup>10</sup> we write the equation for the non-periodic case:

$$\begin{aligned} & (\hat{h}_{KS\sigma} - \varepsilon_{i\sigma})\psi_{i\sigma}^* \\ & = -[V_{xc\sigma} - U_{xc\sigma} - (\bar{V}_{xc\sigma} - \bar{U}_{xc\sigma})]\varphi_{i\sigma}^* \end{aligned} \quad (25)$$

Where  $\psi_{i\sigma}^*$  is the orbital shift<sup>8,10</sup>, and we define:

$$\bar{V}_{xc\sigma} \equiv \int \varphi_{i\sigma}^*(\vec{r}) V_{xc\sigma}(\vec{r}) \varphi_{i\sigma}^*(\vec{r}) d^3r \quad (26)$$

and  $\bar{U}_{xc\sigma}$  is defined as before. It is known<sup>8,10</sup> that when  $V_{xc\sigma}^{OEP}$  is the correct OEP potential the following equation should be fulfilled:

$$S_{\sigma}(\vec{r}) \equiv \sum_{i=1}^{N_{\sigma}} \psi_{i\sigma}^*(\vec{r}) \varphi_{i\sigma}(\vec{r}) + C.C. = 0 \quad (27)$$

The S-iteration approach, suggested by Kümmel and Perdew<sup>10</sup> to solve the OEP equation, is using this property to build an iterative scheme for convergence to the correct OEP  $V_{xc\sigma}^{OEP}$ . In this approach one starts from a guess, typically the KLI solution, for  $V_{xc\sigma}^{OEP}$ , and iteratively update the potential according to:

$$V_{xc\sigma}^{new}(\vec{r}) = V_{xc\sigma}^{old}(\vec{r}) + c \cdot S_{\sigma}(\vec{r}) \quad (28)$$

This procedure is repeated till self consistency is achieved and so  $S_{\sigma}$  becomes zero. This approach has been used for both Fock Exchange and also other orbital dependent functionals such as generalized SIC-OEP<sup>30</sup>. Following the arguments of the BvK cell in the main text - we can easily expand the approach described in equations 25-28 to the periodic case. Following<sup>10</sup> we can define the orbital shift in the periodic case by the perturbation expression:

$$\psi_{ik\sigma}^*(\vec{r}) = - \sum_{j\vec{q}, j\vec{q} \neq ik}^{\infty} \frac{\int \varphi_{ik\sigma}^*(\vec{r}_1) [V_{xc\sigma}(\vec{r}_1) - U_{xc\sigma}(\vec{r}_1)] \varphi_{jq\sigma}(\vec{r}_1)}{\varepsilon_{ik\sigma} - \varepsilon_{jq\sigma}} \times \varphi_{jq\sigma}(\vec{r}) \quad (29)$$

It is easy to show that the integral in 29 is non-zero only for  $\vec{q} = \vec{k}$  and so the orbital shift  $\psi_{ik\sigma}^*(\vec{r})$  retains the  $k$  space symmetry of the orbital  $\varphi_{ik\sigma}^*$ . With this we can now write the periodic analog of equation 25:

$$\begin{aligned} & (\hat{h}_{KS\sigma} - \varepsilon_{ik\sigma})\psi_{ik\sigma}^* = \\ & - [V_{xc\sigma} - U_{xc\sigma} - (\bar{V}_{xc\sigma} - \bar{U}_{xc\sigma})]\varphi_{ik\sigma}^* \end{aligned} \quad (30)$$

It is easier to solve Eq. 30 than to calculate according to Eq. 29 because in Eq. 30 we do not need to calculate empty states. Like the usual Bloch representation we can write  $\psi_{ik\sigma}^* = e^{-i\vec{k}\cdot\vec{r}} \tilde{\psi}_{ik\sigma}^*$  where  $\tilde{\psi}_{ik\sigma}^*$  is periodic over the unit cell. We can then write after taking the complex conjugate:

$$\begin{aligned} & \left( -\frac{(\vec{\nabla} + i\vec{k})^2}{2} + e^{-i\vec{k}\cdot\vec{r}} \hat{V}_{ps,ion} e^{i\vec{k}\cdot\vec{r}} + V_H + V_{xc} - \varepsilon_{ik\sigma} \right) \psi_{ik\sigma}^* \\ & = -[V_{xc\sigma}(\vec{r}) - U_{xc\sigma}(\vec{r})^* - (\bar{V}_{xc\sigma} - \bar{U}_{xc\sigma}^*)] u_{ik\sigma} \end{aligned} \quad (31)$$

Where  $u_{ik\sigma}(\vec{r})$  is simply the lattice periodic Bloch wave function defined earlier by:  $\varphi_{ik\sigma}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{ik\sigma}(\vec{r})$ . we write, in a similar fashion to equation 27, the expression for  $S_{\sigma}$ :

$$\begin{aligned}
 S_{\sigma}(\vec{r}) &\equiv \sum_{i,\vec{k}} \psi_{i\vec{k}\sigma}^*(\vec{r}) \varphi_{i\vec{k}\sigma}(\vec{r}) + C.C. \\
 &= \sum_{i,\vec{k}} \tilde{\psi}_{i\vec{k}\sigma}^*(\vec{r}) u_{i\vec{k}\sigma}(\vec{r}) + C.C. \quad (32)
 \end{aligned}$$

With this expression for  $S_{\sigma}(\vec{r})$  we now repeat the iterative approach outlined in Eq. 28 till self consistency is achieved.

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