

Optimized Effective Potential Method for Polymers

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The optimized effective potential (OEP) method allows for calculation of the local, effective single particle potential of density functional theory for explicitly orbital-dependent approximations to the exchange-correlation energy functional. In the present work the OEP method is used together with the approximation due to Krieger, Li and Iafrate (KLI). We present the first application of this method to polymers. KLI calculations have been performed for the insulating polyethylene and the results have been compared to those from other orbital-dependent potentials. Various properties of the band structure are also calculated. The single-particle band gap strongly depends on the basis set with larger basis sets yielding narrow gaps. For certain physical quantities such as the total energy and the exchange energy, the various orbital-dependent exchange-only and Hartree-Fock results differ only slightly. For the highest occupied orbital energy the difference is more pronounced. In order to get the right band gap in OEP the exchange contribution to the derivative discontinuity is calculated and added to the Kohn-Sham gap. The corrected gap obtained by the KLI approach is 12.8 eV compared with the Hartree-Fock and experimental values of 16.6 and 8.8 eV, respectively. We observe, however, the strong dependence of the derivative discontinuity on the basis set.

1. Introduction

The optimized effective potential (OEP) method was invented by Talman and Shadwick [1], following the original idea of Sharp and Horton [2]. In the now classic OEP approach a given total energy functional depending explicitly on single-particle orbitals is minimized under the constraint that these orbitals are solutions of a single-particle Schrödinger equation with a local, effective potential. The exchange-only OEP can be interpreted as the implementation of the exact exchange-only density functional theory (DFT) [3,4]. Very recently OEP is extended to include electron correlation effects via perturbation theory [5,6]. In this theory both the correlation energy and the potential are expanded using standard perturbation theory. In this way a self-consistent parameter-free KS *ab initio* scheme can be given. The exact energy functional and the exchange-correlation potential provided by the Hohenberg-Kohn theorem can be calculated order-by-order by means of the OEP perturbation theory [6].

To the best of our knowledge, full OEP calculations

have so far only been performed for atoms [4,8] and for semiconductors [9] at the exchange-only level of the theory. The incorporation of electron correlation effects into the OEP formalism has been the subject of few studies [4,10]. Most of these studies, however, have used the complicated self-energy formalism.

To reduce the numerical complexity of the OEP method, Krieger, Li and Iafrate (KLI) introduced a remarkably accurate analytical approximation to OEP and transformed the original OEP equations into an easily manageable form [7]. Applications to atoms and to solids show that the KLI method yields results that are nearly identical to those of OEP [8,11]. The KLI method has been successfully applied for molecules [12] and for certain semiconductors [13,14] using pseudopotentials.

In our previous study we have carried out calculations by means of various orbital-dependent exchange potentials which are accurate approximations of OEP and require less computational effort [15]. We found that the various orbital dependent potentials provide a narrow DFT gap for polyethylene (PE). KS theory will typically give too narrow valence bands and too compressed conduction bands [11]. The KS theory will only give an exact result for the highest occupied energy eigenvalue, therefore, calculated states will in general not have the desired accuracy as one might hope [3,7]. In addition to this, it has been shown that the difference between the highest occupied and lowest unoccupied DFT eigenvalues in the N -electron system (which is what is usually called the DFT band gap) is not the true quasiparticle band gap, but differs from it by the discontinuity in the exchange-correlation potential when an electron is added to the system [4,23]. Therefore, the so-called derivative discontinuity corrections must be taken into account in order to get the right gap [4,15,22]. Consequently, it is desirable to calculate the band structure using the KS method, and then simply add on a single-shot correction to all states [11,15]. In this way much better agreement is found with the Hartree-Fock gap when the exchange corrections are considered to the KS eigenvalue band gap [15]. None of the state-of-the-art exchange-correlation functionals depending only explicitly on the density show the above-mentioned discontinuity in the exchange-correlation potential and therefore do not yield the correct values for the band gaps of the insulating solids [11].

In the last decades quite a number of publications

appeared on polymer electronic structure using mainly Hartree-Fock *ab initio* methods [24]. Results are reported only in recent years, however, using DFT methods like local density approximation (LDA) [26]. The generalized gradient approximation (GGA) [21] resulted in only modest improvement over LDA gap in semiconductors [27].

In this paper, we briefly review the theory of OEP and KLI methods. This work can be taken as the systematic continuation of our previous work on polymer electronic structure obtained by various orbital dependent local exchange potentials [15]. Particular attention is paid to the correction of the OEP eigenvalue band gap. We will present the first results obtained by the KLI orbital dependent exchange potential for polymers. We give the calculated band gaps, band widths, band structures and total energy of polyethylene within the Kohn-Sham density functional scheme using various orbital dependent exchange potentials.

2. Basic Formalism

The following spin-restricted Kohn-Sham type mean-field approach is employed for polymers (the extension of the theory for spinpolarized problems is straightforward):

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]u_i(\mathbf{r}) = \epsilon_i u_i(\mathbf{r}) \quad (1)$$

where $\{u_i(\mathbf{r})\}$ are the single particle orbitals and $v_s(\mathbf{r})$ is the Kohn-Sham effective single particle potential [3].

$$v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \quad (2)$$

The Kohn-Sham one-body potential contains the external, Hartree and exchange-correlation potential. $v_{ext}(\mathbf{r})$ represents the Coulomb potential of the nuclei. $v_H(\mathbf{r})$ is the classical Coulomb repulsion of the electron charge density. The exchange-correlation potential $v_{xc}(\mathbf{r})$ is a nonclassical term. It is formally defined as functional derivative of the exchange-correlation energy $E_{xc}[\rho]$:

$$v_{xc}(\mathbf{r}, [\rho]) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \quad (3)$$

We seek an expression which contains the exact exchange potential and correlation can be added easily on top of the exact exchange-only theory using approximate correlation energy functionals [3]. It must be emphasized, however that the correlation energy functionals either in their local or gradient corrected form may not work in combination with exact exchange. This is because basically all common correlation functionals do not have a long-range component in the corresponding correlation hole (the combined exchange-correlation hole is typically short-ranged). The Colle-Salvetti gradient corrected correlation functional [28], which provided excellent results

for atoms, performed rather badly for molecules for the abovementioned reason [8,12]. Approximate correlation functionals which are derived from the homogeneous or inhomogeneous electron gas model or obtained non-empirically from sum-rule conditions [16] have an incorrect long-range tail (only dynamical correlation is accounted for). The correlation energy functionals provide improper local behaviour in the bond midpoint regions in molecules [16,19,20] which is mainly due to the lack of non-dynamical correlation effects [16]. Therefore, in those methods which work with exact exchange (HF and OEP) the correlation effect can only be accounted for in a more complicated way than in the so-called second generation of DFT [15].

In the optimized effective potential method (OEP) in contrast to the ordinary DFT, the exchange-correlation energy is approximated as an explicit functional of orbitals and only implicit functional of the electronic density [12]. The starting point of the OEP method is the total energy functional

$$E_{tot}^{OEP}[\rho] = \sum_{i=1}^{occ} \int d\mathbf{r} u_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 \right) u_i(\mathbf{r}) + \int d\mathbf{r} \rho(\mathbf{r}) v_{ext}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}^{OEP}[\{u_i\}]. \quad (4)$$

We make use of the chain rule for functional derivatives to obtain from Eq. (3)

$$v_{xc}^{OEP}(\mathbf{r}, [\rho]) = \sum_{i=1}^{occ} \int d\mathbf{r}' \frac{\delta E_{xc}^{OEP}[\{u_i\}]}{\delta u_i(\mathbf{r}')} \frac{\delta u_i(\mathbf{r}')}{\delta \rho(\mathbf{r})} + c.c. \quad (5)$$

where formally $\{u_i[\rho]\}$ are the orbitals which are, however, implicit functionals of the density. Applying the functional chain rule again and after some algebra one obtains the following integral equation:

$$\sum_{i=1}^{occ} u_i(\mathbf{r}) \int d\mathbf{r}' [v_{xc}(\mathbf{r}') - v_i(\mathbf{r}')] G_{si}(\mathbf{r}, \mathbf{r}') u_i^*(\mathbf{r}') + c.c. = 0 \quad (6)$$

where

$$v_i(\mathbf{r}) = \frac{1}{u_i^*(\mathbf{r})} \frac{\delta E_{xc}^{OEP}[u_i]}{u_i(\mathbf{r})} \quad (7)$$

and

$$G_{si}(\mathbf{r}, \mathbf{r}') = \sum_{k \neq i}^{\infty} \frac{u_k(\mathbf{r}) u_k^*(\mathbf{r}')}{\epsilon_i - \epsilon_k}. \quad (8)$$

The integral in Eq. (6) is the fundamental expression for v_{xc} in OEP and can be shown to be equivalent to Eq. (3) [4]. There is no known analytic solution for $v_{xc}[\{u_i\}]$. Therefore, only numerical solutions are

available for spherical atoms [1,4,7,29,30] and for solids [9,13,14] using atomiclike wave functions and assuming integer atomic occupation numbers within each muffin-tin sphere (linear augmented plane-wave method) [11]. These numerical solutions of Eq. (6) are confined to the exchange-only OEP and correlation has been taken into account only via approximate local functionals [9]. In the work of Krieger and co-workers the OEP integral equation is analyzed and a simple approximation is made which reduces the complexity of the original OEP equation significantly and at the same time keeps many of the essential properties of OEP unchanged [7]. Krieger, Li and Iafate gave an exact expression transforming the OEP integral equation (6) into a manageable form. They obtained the following, still *exact* expression for $v_{xc}(\mathbf{r})$:

$$v_{xc}^{OEP}(\mathbf{r}) = v_{xc}^S(\mathbf{r}) + \sum_{i=1}^{occ-1} \frac{\rho_i(\mathbf{r})}{\rho(\mathbf{r})} (\bar{v}_{xci}^{OEP} - \bar{v}_i) + \frac{1}{2} \sum_{i=1}^{occ} \frac{\nabla[p_i(\mathbf{r})\nabla u_i(\mathbf{r})]}{\rho(\mathbf{r})}, \quad (9)$$

$$\bar{v}_i = \int d\mathbf{r} \rho_i(\mathbf{r}) v_i(\mathbf{r}),$$

where $m = occ$ is the highest occupied one electron energy level. $\rho_i = |u_i|^2$ is the partial density. $v_x^S(\mathbf{r})$ is the Slater's potential (its correlation part is not known exactly)

$$v_x^S(\mathbf{r}) = \frac{1}{2\rho(\mathbf{r})} \int d\mathbf{r}' \frac{|\gamma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}, \quad (10)$$

where $\gamma(\mathbf{r}, \mathbf{r}')$ is the first-order density matrix. The summation runs over the orbital index for all the occupied orbitals up to the highest occupied m th orbital (Fermi level). The function p_i is defined by

$$p_i(\mathbf{r}) = \frac{1}{u_i(\mathbf{r})} \int d\mathbf{r}' [v_{xc}^{OEP}(\mathbf{r}') - v_i(\mathbf{r}')] G_{si}(\mathbf{r}, \mathbf{r}') u_i(\mathbf{r}'). \quad (11)$$

In practical applications the last term in Eq. (9) turned out to be quite small in atomic systems and has small effect only on the atomic shell boundaries [7]. This additional term's average over the m th orbitals is zero [7]. Neglecting this term one obtains the exchange-only KLI-approximation which, after some algebra, can be written in the following form [7]

$$v_x^{KLI}(\mathbf{r}) = v_x^S(\mathbf{r}) + \sum_{i=1}^{occ-1} \frac{|u_i(\mathbf{r})|^2}{\rho(\mathbf{r})} \sum_{j=1}^{occ-1} (\mathbf{A}^{-1})_{ij} (\bar{v}_{xj}^S - \bar{v}_{xj}). \quad (12)$$

$$\mathbf{A}_{ji} = \delta_{ji} - \mathbf{M}_{ji}, \quad (13)$$

$$\mathbf{M}_{ji} = \int \frac{\rho_j(\mathbf{r})\rho_i(\mathbf{r})}{\rho(\mathbf{r})} d\mathbf{r}, i, j = 1, \dots, m-1. \quad (14)$$

\bar{v}_{xj}^S and \bar{v}_{xj}^{HF} can be given as follows:

$$\bar{v}_{xj}^S = \int \rho_j(\mathbf{r}) v_x^S(\mathbf{r}) d\mathbf{r}. \quad (15)$$

$$\bar{v}_{xj} = -\frac{1}{2} \sum_{i=1}^{occ} \int d\mathbf{r} d\mathbf{r}' \frac{u_i^*(\mathbf{r}) u_j^*(\mathbf{r}') u_i(\mathbf{r}') u_j(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}, \quad (16)$$

Atomic calculations [8] show that in all situations, the KLI potential mimics the OEP results extremely well and even correctly preserves the property of integer discontinuity [4,11]. Moreover, the KLI method is also easy to program. In this article we restrict ourself to various exchange-only methods, however, the extension of these methods to exchange-correlation case is straightforward using the best available correlation energy functional.

For the constants $w_i = \bar{v}_{xi}^{OEP} - \bar{v}_i$ (Eq. (9)) an alternative expression is proposed by Gritsenko *et al.* [19] in terms of orbital energies ϵ_i . It follows from gauge invariance requirements, proper scaling and short range behaviour of the response part of Eq. (13) that w_j can only depend on an energy difference. In their work Eq. (13) is approximated by:

$$v_x^{SSP}(\mathbf{r}) = v_x^S(\mathbf{r}) + \frac{8\sqrt{2}}{3\pi^2} \sum_{i=1}^{occ-1} \frac{|u_i(\mathbf{r})|^2}{\rho(\mathbf{r})} \sqrt{\epsilon_F - \epsilon_i} \quad (17)$$

We use the notation SSP (Slater's potential + step potential) for this exchange potential. The parameter $\frac{8\sqrt{2}}{3\pi^2}$ is determined from the homogeneous electron gas (HEG) model and therefore Eq. (17) is exact in the HEG limit [19]. This constant is chosen as universal parameter for all the calculations. The main advantage of this expression is that one can avoid the matrix inversion of Eq. (12). Note that the summation runs over all the occupied orbitals except the highest one like in Eq. (12). With the step potential-like second term v_x^{SSP} provides a good approximation to the OEP exchange-potential [19].

In actual calculations we used the following iterative scheme for getting v_x^{KLI} instead of Eq. (12) in each k th SCF cycle

$$v_x^{KLI(k+1)}(\mathbf{r}) = v_x^{S(k)}(\mathbf{r}) + \sum_{i=1}^{m-1} \frac{\rho_i^k}{\rho^k} (\bar{v}_x^{KLI(k)} - \bar{v}_i^k). \quad (18)$$

The initial guess for Eq. (18) is chosen as follows

$$v_x^{KLI(0)}(\mathbf{r}) = \frac{1}{2} (v_x^{LDA}(\mathbf{r}) + \frac{2}{3} v_x^S(\mathbf{r})). \quad (19)$$

We found this particular form of the initial guess is close to the KLI exchange potential.

The KLI approximation to OEP provides a self-interaction free exchange potential and proper $-\frac{1}{r}$ asymptotics as $r \rightarrow \infty$. The approximate potentials v_x^S and v_x^{SSP} exhibit proper asymptotics as well [19]. LDA or GGA exchange potentials do not show the correct asymptotic behaviour [7]. For instance, while the popular GGA exchange-correlation energy functional [21] provides energies for atoms with nice agreement with the exact results, the exchange-correlation potentials and the energy eigenvalues of the highest occupied state, are both suffering from error [6,7]. Nevertheless, various forms of GGAs are of great importance and further developments can certainly be expected in this field in the next future [39].

3. Computational details

Closed shell exchange-only KLI calculations have been performed for polyethylene and the results are compared with those from the Hartree-Fock and Slater approach. For all the calculations a new code is used which has been developed in our laboratory [33]. The various one and two-electronic integrals are taken from the Erlangen periodic Hartree-Fock program [32]. During the calculations the number of k -points is set to 25. The SCF iterations are continued until the density matrix elements changed by less than 10^{-5} . 876 and 778 grid points are used for heavy atoms and for hydrogen in the numerical integration using Becke's fuzzy cell method [45]. Thus the total number of grid points per unit cell is 2432. Further computational details of our implementation of polymeric calculations are given elsewhere [15]. For polyethylene the experimental "zig-zag" geometry is used [26]. Since the various properties of polyethylene depend significantly on the geometry, we give the structure we have used for our calculations: the C-C and C-H bond lengths are set to 1.54 and 1.10 Å while for the CCC, HCH and HCC angles 113, 108 and 113 degrees are used. Recent geometry optimization calculations with various DFT functionals provided values in very nice agreement with these experimental bonding parameters [35]. Two types of bases are used: the Clementi's minimal (7S/3P) and the larger double- ζ (9S/5P) basis sets for carbon and the 4S and 6S for hydrogen atom, respectively [36]. The (11S/7P) basis set is also employed in certain cases. To make comparison with previously published atomic and molecular results [8,12] and also to check the reliability of our code we have made calculations in the atomic and molecular limit. To do so, we set the translation vector to roughly 20.0 a.u. and choose the interaction only between the nearest-neighbour CH_2 unit cells [24]. Using these parameters the computed properties must be very close to those obtained by atomic or molecular codes. The test provides nice agreement with atomic calculations ob-

tained by Hartree-Fock, Slater's, KLI or SSP exchange-only method which confirms the reliability of our code. Further computational details of our implementation of KLI for polymers are given elsewhere [15].

4. Results

The comparison is carried out for Be, LiH and for N_2 [12,19] in the molecular limit and the energetical results are summarized in Table I. For the total energy we obtained -14.569 , -14.562 , -14.568 a.u. for Be using HF, Slater and KLI methods (with Clementi's minimal basis set). The deviation from HF can be compared with results obtained by others [19]: 7 and 1 mHartree for Slater and KLI, while Gritsenko *et al.* obtained 11 and 0.0, respectively. For LiH the corresponding numbers are: -7.9543 , -7.9542 , -7.9542 a.u. The deviations: 0.0, 0.0 mH, while Grabo *et al.* [12] found 6 mH for Slater. The discrepancy between our and other results can be considered rather small and is probably due to the different basis set applied here. For LiH the highest occupied orbital energies are as follows: $-.2914$, $-.3228$ and $-.3227$ a.u. which are compared with Grabo's values [12], $-.3017$ (HF), $-.3150$ (Slater) and $-.3011$ (KLI). Finally we give the test of our code for H_2 as well. For two-electronic systems the results obtained by HF or KLI must be identical [12]. For E_{tot} and ϵ_m (total energy and highest occupied energy level) the values -1.12796 , -1.127953 and $-.5948$, $-.5913$ a.u. are obtained by HF and KLI, respectively. The small difference must be attributed to numerical inaccuracy in the numerical integration (KLI). Results are also given for N_2 in Table I. The KLI total energy for N_2 differs from the HF one by 9 mH which is comparable with that obtained by a fully-numerical basis-set-free code [12].

Our results for some physical properties of polyethylene are shown in Tables II-III. The results are listed in terms of the order of the neighbouring interaction. Actually, it turns out that at least 5 neighbours are necessary in order to get convergent results for all the physical properties we are interested in within the finite neighbouring approach [15]. For comparison we have calculated all the properties at higher number of neighbouring cells [15].

Our calculation using the large (11S/7P) basis set provides a deeper Hartree-Fock total energy (-39.02326 a.u.) than the one obtained by Suhai [44] using the 6-31G* basis set (-39.02251 a.u.). According to the expectations the comparison of total energies shows us that Hartree-Fock provides the deepest energies while the various Kohn-Sham schemes result in somewhat higher energies. In principle the total energy is always lower in HF than in (exchange-only) OEP since the use of a local potential imposes one more variational constraint on the orbitals [4]. In general, the following inequality holds:

$E_{HF} < E_{OEP} < E_{KLI} < E_{LDA}$ [18]. KLI is always an upper bound to OEP and always lower than E_{LSDX} (local exchange-only spin-density theory). The difference is around 10 mH for KLI. For molecules T. Grabo and E. K. U. Gross [12] found differences around 7-8 mH for KLI. For a larger basis set KLI and HF total energies differ from each other more significantly (23 mH), which is much smaller, however, than the corresponding difference for Slater (44 mH). We believe that the bulk part of the difference is not due to the approximate nature of the exchange potentials applied here, but to the different nature of Hartree-Fock and DFT approaches in accordance with earlier studies [7,12]. These results must be compared with the values obtained by calculations in the molecular limit [12]. Treating the CH_2 unit cell in the molecular limit (Table I), one can see that all the properties (total energy, one electron energies) are close to the Hartree-Fock values. However, in polymer calculations we got for the one electron energies quite significant deviation from the Hartree-Fock values (Tables II-III): employment of local exchange potentials generally leads to higher Fermi level and and at the same time to lower first virtual levels. Therefore, the single particle band gap of polyethylene is smaller for the KS methods than for HF.

We also observe the peculiar behaviour of the highest occupied orbital energies ϵ_m obtained by KLI, which differ from HF values significantly and are closer to $\epsilon_m^{X\alpha}$ [15]. This latter result is rather surprising since atomic and molecular calculations show that the ϵ_m values are very close to those obtained by HF or OEP [7,8,12]. Also, in HF we found no big difference between the highest occupied orbital energy in the molecular limit and in the infinite system. While this comes as a surprise we attribute the increase of the Fermi level due to periodic effects, which come into play only, when one employs localized exchange-potentials for infinite systems. One can follow how the periodic effect comes into play when the change of ϵ_m is examined in terms of the order of the neighbouring interaction in Table II-III. As may be read from Table II-III., when $neig = 1$, ϵ_m obtained by Slater or KLI is the lowest one, however, when $neig$ increased the Fermi level is getting closer to zero progressively. Hartree-Fock does not produce such a phenomenon since it has a *non-local* orbital dependent exchange-potential, which is always deeper than the local counterpart, and thus is keeping the Fermi level at a deeper energy level. However, using the largest basis set in this study (11S/7P) we obtained somewhat higher ϵ_m^{HF} (Table III) as well. As may be seen from Table III, by increasing the number of neighbours and the basis set ϵ_m^{KLI} moves upward significantly and becomes higher than the corresponding LDA value of -0.242 a.u. [15], except for SSP. As can be seen in Tables III, increasing the basis set reduces the calculated KS gap for all the methods, which is mainly due to the lowering of the first virtual level ϵ_{m+1} and to the upward

movement of ϵ_m . While the HF single-particle gap is still too wide (16.6 eV), the calculated Slater's and KLI eigenvalue gaps are too narrow (3.4 and 5.1 eV). Others reported the value of 16.7 eV for the HF gap quite close to our value [40]. It is worth to note, however, that other calculations with 6-31G** basis set resulted in the smaller 13.4 eV for the HF gap [44]. Recent reports proved that the band gap strongly depends not only on the basis set but also on the quality of the finite neighbour approach [40].

It is known [42] that the exact exchange-correlation potential exhibits a discontinuous jump as the number of electrons passes through an integer. This derivative discontinuity plays an important role in the calculations of the exact band gap which can be written as

$$\begin{aligned} \Delta &= \Delta_{nonint}^{KS} + \Delta_{xc} \\ &= \epsilon_{N+1}^{KS}(N) - \epsilon_N^{KS}(N) + \Delta_{xc} \quad , \end{aligned} \quad (20)$$

where N is the number of electrons, Δ_{KS}^{nonint} is the Kohn-Sham band gap and Δ_{xc} is the derivative discontinuity. For continuum approximations like LDA or GGA this discontinuity vanishes. However, in OEP as well as in our (orbital-dependent) approximations to OEP, the discontinuity is finite [4,15,22]. The exchange-only contribution to the band gap, Δ_x , is given by [9,22]

$$\begin{aligned} \Delta_x(i \rightarrow \nu) &= \langle u_\nu | \hat{v}_x^{HF} - \hat{v}_x^{OEP}[\rho] | u_\nu \rangle \\ &\quad - \langle u_i | \hat{v}_x^{HF} - \hat{v}_x^{OEP}[\rho] | u_i \rangle \\ &\quad - \langle \nu i | \nu i \rangle - 2 \langle \nu i | i \nu \rangle, \end{aligned} \quad (21)$$

with \hat{v}_x^{HF} being the nonlocal HF exchange operator, however, constructed from the $N/2$ occupied KS orbitals. In our previous study [15] we have calculated Δ_x using Slater and SSP methods and the results can also be seen in Table II-III. The last two terms on the r.h.s. of Eq. (20) will vanish for systems with periodic boundary conditions and an infinite number of unit cells [9]. Since we only take a finite number of cells into account, we will also get contributions to Δ_x from these terms. We have studied the convergence of Δ_x and, for a given basis set, at $neig = 5$ the discontinuity seems to be poorly converged with respect to the basis set and the results have to be read with due caution. In principle the discontinuity is guaranteed to be smaller than the true band gap by its definition [4]. However, calculations do not confirm this expectation for semiconductors [9]. Nevertheless, Δ_x brings the KS gap somewhat closer to the HF one. With the minimal basis set Δ_x represents a rather small correction to the band gap and actually is negative (Table II). This is in contrast with the finding that Δ_x amounts to typically twice the band gap [9]. However, the situation changes completely when a larger basis set is used (Table III). The corrected band gap obtained by the larger basis set with the KLI method (Table III) is 12.8 eV while the Slater and SSP approach yield 9.7 and 12.7 eV, respectively [15].

The much more involved second-order self-energy calculations resulted in 10.3 eV for the quasi-particle (QP) band gap [24,44]. Further corrections to Δ would certainly result in a gap close to the QP and experimental values. According to the expectations KLI and SSP provide values not far from the HF one while the naked Slater potential yields somewhat higher band gap than the experimental value of 8.8 eV [24,38]. In the basis set limit one expects the KLI gap to be close to the HF value. The discrepancy between the KLI gap and the experimental one must be partly attributed to the correlation contribution to the derivative discontinuity (Δ_c). It is also useful to make comparison with quasi-particle calculations where one corrects the HF single-particle gap to get the quasi-particle band structure [24,40,44]. According to the results of Suhai obtained for polyethylene [44] the QP correction reduced the HF gap from 15.0 eV to 10.3 eV while the derivative discontinuity correction raises the OEP gap from 5.1 eV up to 12.8 eV. It would be rather interesting to add on further corrections to Δ_x including correlation at second order level of theory [22]. However, these kind of calculations are beyond the scope of the present article.

Atomic calculations provided KLI eigenvalues which are very close to the HF and OEP values [8]. In molecules, however, Grabo *et al.* found slight deviations from the HF values [12]. Approximate OEP calculations on polyethylene also resulted in eigenvalues different from HF [15]. In Table II-III we have already demonstrated that this is true in the KLI approach as well. In order to make a more detailed analysis of this problem we give the one-electron energies obtained by HF and KLI exchange-only methods in Table IV. We compare the HF and KLI eigenvalues obtained in the molecular limit and in the polymer. In general HF provides deeper eigenvalues by 100 to 200 mH for the core orbitals and much less difference for the valence orbitals. The reverse is true for the KLI virtual orbital energies. The KLI ϵ_m value of -0.093 eV is compared with the values of -0.379 and -0.242 eV obtained by HF and LDA [15], respectively. To sum up, the KLI eigenvalues shift upward in the valence region and shift downward in the virtual space when compared with the HF values in the polymer. The KLI highest occupied orbital energy is rather close to the HF one in the molecular limit. The differences are around 15 and 100 mH, in the molecule and in the polymer.

The exchange energies are also presented for various methods. KLI produces a higher exchange energy than HF by some 30 mH. The reason for this has to be found in the different form of the virial theorem which holds for HF and for DFT. In DFT the virial theorem is as follows [37],

$$E_x[\rho] = \int d\mathbf{r}[3\rho(\mathbf{r}) + \mathbf{r}\nabla\rho(\mathbf{r})]v_x(\mathbf{r}), \quad (22)$$

On the basis of Eq. (22) deeper exchange-potential will

provide deeper exchange energy for the same density. Among the model potentials employed in this study the Slater potential exhibits the deepest potential curve in atoms [7,11] and in Table III one can see that the exchange energy E_x^{Slater} is the deepest and differ from Hartree-Fock by some 50 mH. KLI provides exchange potential similar to that of LDA [19,11] in magnitude, although the shape of the curves are different (see e.g. in refs. [7,11]). The Fermi level ϵ_m is deepest for the Slater's potential among the KS-based methods due to the deepest exchange potential. Even the first virtual level dropped below zero as obtained by the largest basis set by the Slater's exchange potential. The exchange energy obtained by this potential is approximately by 1% lower than the Hartree-Fock exchange energy. This difference is around the magnitude of the non-dynamical correlation energy [16]. Therefore the Slater's potential is a suitable candidate for further calculations together with the commonly used correlation energy functionals which account for only the short range type dynamical correlation energy. The success of the popular exchange energy functionals, such as the one of Becke [45] and the GGA's [21] lie in the overestimation of Hartree-Fock exchange and therefore in the effective treatment of exchange-correlation mainly due to the cancellation of errors with opposite signs [16]. On the basis of Table III v_x^{SSP} provides the best agreement either with the Hartree-Fock total energy or with the exchange energy. Therefore one might speculate that the SSP potential is somewhat closer to the exact OEP potential than to the KLI potential. The v_x^{SSP} is the functional not only of the orbitals but also of the eigenvalues of the KS problem while v_x^{KLI} is only of the orbitals. Further steps in this direction can be desirable in the future in developing a general and accurate potential $v_{xc}^{OEP}[\{u_i, \epsilon_i\}]$ [6] which is a functional of the eigensolutions of the KS problem.

In Fig. 1 the band structure is plotted obtained by various methods using the Clementi's double- ζ basis. One can see that virtual bands are appearing below the zero energy level obtained only by the Slater potential. Note that the first three curves in both of the figures are the occupied valence energy levels (Fig. 1 and 2, respectively, the lowest, core level is not plotted). We also note from Fig. 1 that the highest three virtual levels are similar to the virtuals obtained by the minimal basis set (see Fig. 1 in ref. [15]). However, new patterns appear for the first two virtual levels as obtained by the larger basis set (plotted with dashed lines on Fig. 1). The lowest transition from the Fermi level to the first virtual is appearing at the edge of the Brillouin zone ($k = 1$). However, around $k = 0.5$ one can see quasi-degeneracy of certain bands or even crossing of virtual levels close to the edge of the Brillouin zone.

The maximum of the valence band is appearing in the range of $[-2, -11]$ eV with the lowest and highest values

for KLI and Hartree-Fock, respectively, compared to the experimentally suggested values of ionization potential of 9.6 – 9.8 eV [38]. Others give lower experimental values in the 7.6 – 8.8 eV range [24,25]. KLI provides the much lower 2.3 eV value while Slater and SSP give 7.6 and 4.4 eV [15], respectively. By density functional linear muffin-tin orbital method the value of 5.1 eV is obtained for helical polyethylene [25]. The calculated lowest valence band widths for $X\alpha$, HF, SSP, Slater's and KLI approach are 6.2, 9.0, 4.0, 3.6 and 3.9 eV respectively, which are to be compared with the experimental 7.2 eV [38]. The total valence bandwidths are 14.0 eV ($X\alpha$), 15.4 eV (SSP), 15.6 eV (KLI) and 19.8 eV (HF), compared to a experimental value of 16.2 eV [38]. Slater, KLI and SSP perform quite well for this band width. The calculated gap between the lowest valence band and the minimum of the higher valence bands is 3.3 eV (HF), 1.9 eV ($X\alpha$), 3.0 (SSP), 3.2 (Slater) [15] and 2.8 eV (KLI) compared with the experimental 2.0 eV [38]. The HF and $X\alpha$ values are in accordance with those obtained by others [24,26]. The bottom of the valence band with σ symmetry is 18.0 eV obtained by KLI which is compared with the HF (31.0 eV) and Slater (23.6) eV values. The overall conclusion can be drawn that the various orbital dependent potentials provide band structures similar to one another and all of them differ from HF. The largest deviation from experiment is found for the lowest valence band width (LVBW) which is rather narrow in the OEP methods. HF give too wide LVBW while $X\alpha$ -LDA yields a value in closest agreement with experiment.

Conclusions

Density functionals of the third generation treat both the kinetic and exchange energy exactly at the orbital dependent level of the theory. These orbitals come from a local potential and, due to the Hohenberg-Kohn theorem, are therefore functionals of the density. The optimized effective potential method, in the form given by Talman and Shadwick [1] allows one to treat orbital-dependent functionals in the framework of Kohn-Sham density functional theory. The OEP integral equations are difficult to solve for extended systems and therefore several approximations are introduced. Among them the one obtained by Krieger *et al.* (KLI) and another one derived by Gritsenko *et al.* have become known in the last few years.

In this work we have applied the exchange-only KLI approximation to the OEP approach for insulating polymers. Calculations have been carried out for polyethylene with a new polymer code using the efficient KLI approximation to OEP. The results obtained by the "naked" Slater's potential and KLI are compared with

those obtained by Hartree-Fock. The addition of the step-potential as a response part of the exact exchange (Eq. 13) to the Slater's potential considerably improves the quality of various physical properties calculated for polyethylene. To test the quality and reliability of our code we performed calculations in the atomic and molecular limit. The results can be brought into harmony with those obtained by others.

In general, we find that the band structure calculated by different v_x are similar with little qualitative difference, while all of them differ significantly from HF which have valence bands much deeper and much higher virtual levels. The single-particle band gap obtained by the KLI or Slater approaches is too narrow when compared with the experiment. The shifted values are observed for the Fermi level, which differ from Hartree-Fock values significantly. The one electron energy levels are carefully examined and an upward shift of eigenvalues observed when compared with those of HF, and also the counter shift of virtual levels. The deviation from the HF eigenvalues is more significant than in molecules or in atoms. In order to make a valuable comparison with Hartree-Fock, LDA and with the experimental gap, correction must be taken into account to the Kohn-Sham eigenvalue gap. The exchange contribution to the derivative discontinuity is calculated by the KLI exchange potential. In this way the KS single particle gap is corrected by a single shot calculation on top of exchange-only OEP. The exchange contribution to the band gap is somewhat less than twice the KS eigenvalue gap. According to the expectations the corrected gap is much closer to the Hartree-Fock value than the KS eigenvalue gap.

Acknowledgments

This work was supported by the Flemish Science Foundation.

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TABLE I. Comparison of our HF and KLI results (Clementi's double zeta basis) using the code DIOGENES [33] with values from the literature.

E_{tot} and ϵ_m are the total energy and the highest occupied orbital energy in a.u.

		HF ^{our}	HF ^{other}	KLI ^{our}	KLI ^{other}
Be	E_{tot}	-14.569	-14.5730 ^a	-14.5684	-14.5723 ^b
	ϵ_m	-0.3089	-0.3093	-.3092	-.3089
LiH	E_{tot}	-7.954	-7.987 ^b	-7.954	-7.987 ^c
		-7.8629 ^d	-7.8620 ^e		
	ϵ_m	-0.2914	-0.3017 ^b	-0.3227	-0.3011 ^c
		-.2870 ^d	-.2857 ^e		
N_2	E_{tot}	-108.892 ^f	-108.994 ^d	-108.883 ^f	-108.986 ^c
	ϵ_m	-0.6352 ^f	-0.6152 ^c	-0.6659 ^f	-0.6818 ^c
CH_2	E_{tot}	-38.8650 ^f		-38.8632 ^f	
	ϵ_m	-0.3750 ^f		-0.3595 ^f	

^a [7]

^b [8]

^c [12]

^dwith STO-3G basis

^ewith STO-3G basis using Gaussian94 [43] program package

^f The large 11S/7P basis set is used for N_2 and for CH_2 .

Fig. 1 The calculated valence band structure obtained by various exchange-only methods as a function of the dimensionless variable k with $k = 0$ being the zone center and $k = 1$ the zone boundary. The Brillouin zone is that corresponding to a CH_2 unit cell. Solid lines correspond to the occupied levels while the dashed lines to the virtual levels. The two lowest dashed curves of virtual levels are of particular interest (see text). The Clementi's double- ζ basis set is used and 8 neighbours are considered for the CH_2 unit cell.

TABLE II. Calculated properties of polyethylene by various DFT methods using the minimal basis set HF, Slater, SSP and KLI denote the Hartree-Fock, exchange-only method with Slater's potential, Slater's potential with orbital dependent step potential and the KLI exchange-only OEP method. All the properties are in a.u. except the HOMO-LUMO gap which is given in eV. The Clementi's minimal basis set (7S/3P) is used. *Neig* gives the number of neighbouring cells taken into account. E_{tot} , E_x are the calculated total and exchange energies per CH_2 unit cell. Δ_x is the exchange component of the derivative discontinuity. The calculations are carried out for the CH_2 unit cell.

neig		HF	Slater ^a	SSP ^a	KLI
1	E_{tot} (a.u.)	-39.03535	-39.01888	-39.02768	-39.02042
	E_x (a.u.)	-5.82128	-5.84774	-5.79080	-5.7713
	ϵ_m (a.u.)	-.6672	-.5634	-.4924	-.3524
	ϵ_{m+1} (a.u.)	.3978	.0074	-.1084	.2228
	gap (eV)	29.0	15.1	16.4	15.7
	Δ_x (eV)		-5.7	-4.4	-3.2
5		-38.88012	-38.86891	-38.87278	-38.86981
		-5.75048	-5.76397	-5.7379	-5.7297
		-.4747	-.3524	-.2312	-.0871
		.3444	-.0433	.1310	.2786
		22.3	8.4	9.9	10.0
			-3.5	-1.9	-1.2
8		-38.88008	-38.86890	-38.87275	-38.86954
		-5.75049	-5.76400	-5.7378	-5.7284
		-.4760	-.3518	-.2318	-.0972
		.3436	-.0425	.1303	.275
		22.3	8.4	9.9	10.1
			-3.5	-1.9	-1.1
	KS gap+ Δ_x		4.9	8.0	9.0

^a [15]

TABLE III. Calculated properties of polyethylene by various DFT methods using the Clementi's double-zeta basis set (9S/5P).

Results with basis (11S/7P) are also given in the bottom of the Table. The sum of the calculated KS eigenvalue gap Δ_{nonint}^{KS} and the exchange derivative discontinuity Δ_x is also given together with the exchange-only LDA and experimental gap (eV). The notations are the same as in Table I.

neig		HF	Slater ^a	SSP ^a	KLI
5	E_{tot}	-39.01068	-38.96683	-38.99704	-38.99311
	E_x	-5.8783	-5.9368	-5.8841	-5.8405
	ϵ_m	-.4049	-.2951	-.1628	-.1023
	ϵ_{m+1}	.1489	-.1590	-.0007	.0284
	KS gap	15.1	3.7	4.4	3.6
	Δ_x		3.4	3.8	1.9
8	(9S/5P)	-39.01056	-38.96684	-38.99760	-38.99407
		-5.8780	-5.9367	-5.9036	-5.8621
		-.3984	-.2774	-.1130	-.0997
		.1558	-.1655	-.0755	.0322
		15.1	3.7	4.4	3.6
			3.2	3.7	2.4
8	(11S/7P)	-39.02326	-38.99926	-39.01361	-39.00701
		-5.8977	-5.9486	-5.9036	-5.8553
		-.3786	-.2401	-.1130	-.0933
		.2320	-.1151	.0755	.0958
		16.6	3.4	5.1	5.1
			6.3	7.6	7.7
	KS gap+ Δ_x		9.7	12.7	12.8
	LDA				7.6 ^a
	EXP				8.8 ^b

^a [15]

^b [24,38]

TABLE IV. One-electron energies (a.u.) obtained by HF and KLI exchange-only approaches using the Clementi's (11S/7P) basis set and 8 neighbours for polyethylene ($k = 1$)

	HF ^{mol}	KLI ^{mol}	HF ^{poly}	KLI ^{poly}
ϵ_1	-11.289	-10.201	-11.219	-9.820
ϵ_2	-.904	-.774	-.800	-.511
ϵ_3	-.587	-.537	-.681	-.401
ϵ_4	-.375	-.359	-.379	-.093
ϵ_5	.056	-.318	.232	.096
ϵ_6	.240	-.058	.232	.109
ϵ_7	.314	-.005	.392	.301
ϵ_8	.518	.192	.719	.527

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The optimized effective potential (OEP) method allows for calculation of the local, effective single particle potential of density functional theory for explicitly orbital-dependent approximations to the exchange-correlation energy functional. In the present work the OEP method is used together with the approximation due to Krieger, Li and Iafrate (KLI). We present the first application of this method to polymers. KLI calculations have been performed for the insulating polyethylene and the results have been compared to those from other orbital-dependent potentials. Various properties of the band structure are also calculated. The single-particle band gap strongly depends on the basis set with larger basis sets yielding narrow gaps. For certain physical quantities such as the total energy and the exchange energy, the various orbital-dependent exchange-only and Hartree-Fock results differ only slightly. For the highest occupied orbital energy the difference is more pronounced. In order to get the right band gap in OEP the exchange contribution to the derivative discontinuity is calculated and added to the Kohn-Sham gap. The corrected gap obtained by the KLI approach is 12.8 eV compared with the Hartree-Fock and experimental values of 16.6 and 8.8 eV, respectively. We observe, however, the strong dependence of the derivative discontinuity on the basis set.

1. Introduction

The optimized effective potential (OEP) method was invented by Talman and Shadwick [1], following the original idea of Sharp and Horton [2]. In the now classic OEP approach a given total energy functional depending explicitly on single-particle orbitals is minimized under the constraint that these orbitals are solutions of a single-particle Schrödinger equation with a local, effective potential. The exchange-only OEP can be interpreted as the implementation of the exact exchange-only density functional theory (DFT) [3,4]. Very recently OEP is extended to include electron correlation effects via perturbation theory [5,6]. In this theory both the correlation energy and the potential are expanded using standard perturbation theory. In this way a self-consistent parameter-free KS *ab initio* scheme can be given. The exact energy functional and the exchange-correlation potential provided by the Hohenberg-Kohn theorem can be calculated order-by-order by means of the OEP perturbation theory [6].

To the best of our knowledge, full OEP calculations

have so far only been performed for atoms [4,8] and for semiconductors [9] at the exchange-only level of the theory. The incorporation of electron correlation effects into the OEP formalism has been the subject of few studies [4,10]. Most of these studies, however, have used the complicated self-energy formalism.

To reduce the numerical complexity of the OEP method, Krieger, Li and Iafrate (KLI) introduced a remarkably accurate analytical approximation to OEP and transformed the original OEP equations into an easily manageable form [7]. Applications to atoms and to solids show that the KLI method yields results that are nearly identical to those of OEP [8,11]. The KLI method has been successfully applied for molecules [12] and for certain semiconductors [13,14] using pseudopotentials.

In our previous study we have carried out calculations by means of various orbital-dependent exchange potentials which are accurate approximations of OEP and require less computational effort [15]. We found that the various orbital dependent potentials provide a narrow DFT gap for polyethylene (PE). KS theory will typically give too narrow valence bands and too compressed conduction bands [11]. The KS theory will only give an exact result for the highest occupied energy eigenvalue, therefore, calculated states will in general not have the desired accuracy as one might hope [3,7]. In addition to this, it has been shown that the difference between the highest occupied and lowest unoccupied DFT eigenvalues in the N -electron system (which is what is usually called the DFT band gap) is not the true quasiparticle band gap, but differs from it by the discontinuity in the exchange-correlation potential when an electron is added to the system [4,23]. Therefore, the so-called derivative discontinuity corrections must be taken into account in order to get the right gap [4,15,22]. Consequently, it is desirable to calculate the band structure using the KS method, and then simply add on a single-shot correction to all states [11,15]. In this way much better agreement is found with the Hartree-Fock gap when the exchange corrections are considered to the KS eigenvalue band gap [15]. None of the state-of-the-art exchange-correlation functionals depending only explicitly on the density show the above-mentioned discontinuity in the exchange-correlation potential and therefore do not yield the correct values for the band gaps of the insulating solids [11].

In the last decades quite a number of publications

appeared on polymer electronic structure using mainly Hartree-Fock *ab initio* methods [24]. Results are reported only in recent years, however, using DFT methods like local density approximation (LDA) [26]. The generalized gradient approximation (GGA) [21] resulted in only modest improvement over LDA gap in semiconductors [27].

In this paper, we briefly review the theory of OEP and KLI methods. This work can be taken as the systematic continuation of our previous work on polymer electronic structure obtained by various orbital dependent local exchange potentials [15]. Particular attention is paid to the correction of the OEP eigenvalue band gap. We will present the first results obtained by the KLI orbital dependent exchange potential for polymers. We give the calculated band gaps, band widths, band structures and total energy of polyethylene within the Kohn-Sham density functional scheme using various orbital dependent exchange potentials.

2. Basic Formalism

The following spin-restricted Kohn-Sham type mean-field approach is employed for polymers (the extension of the theory for spinpolarized problems is straightforward):

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]u_i(\mathbf{r}) = \epsilon_i u_i(\mathbf{r}) \quad (1)$$

where $\{u_i(\mathbf{r})\}$ are the single particle orbitals and $v_s(\mathbf{r})$ is the Kohn-Sham effective single particle potential [3].

$$v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \quad (2)$$

The Kohn-Sham one-body potential contains the external, Hartree and exchange-correlation potential. $v_{ext}(\mathbf{r})$ represents the Coulomb potential of the nuclei. $v_H(\mathbf{r})$ is the classical Coulomb repulsion of the electron charge density. The exchange-correlation potential $v_{xc}(\mathbf{r})$ is a nonclassical term. It is formally defined as functional derivative of the exchange-correlation energy $E_{xc}[\rho]$:

$$v_{xc}(\mathbf{r}, [\rho]) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \quad (3)$$

We seek an expression which contains the exact exchange potential and correlation can be added easily on top of the exact exchange-only theory using approximate correlation energy functionals [3]. It must be emphasized, however that the correlation energy functionals either in their local or gradient corrected form may not work in combination with exact exchange. This is because basically all common correlation functionals do not have a long-range component in the corresponding correlation hole (the combined exchange-correlation hole is typically short-ranged). The Colle-Salvetti gradient corrected correlation functional [28], which provided excellent results

for atoms, performed rather badly for molecules for the above-mentioned reason [8,12]. Approximate correlation functionals which are derived from the homogeneous or inhomogeneous electron gas model or obtained non-empirically from sum-rule conditions [16] have an incorrect long-range tail (only dynamical correlation is accounted for). The correlation energy functionals provide improper local behaviour in the bond midpoint regions in molecules [16,19,20] which is mainly due to the lack of non-dynamical correlation effects [16]. Therefore, in those methods which work with exact exchange (HF and OEP) the correlation effect can only be accounted for in a more complicated way than in the so-called second generation of DFT [15].

In the optimized effective potential method (OEP) in contrast to the ordinary DFT, the exchange-correlation energy is approximated as an explicit functional of orbitals and only implicit functional of the electronic density [12]. The starting point of the OEP method is the total energy functional

$$E_{tot}^{OEP}[\rho] = \sum_{i=1}^{occ} \int d\mathbf{r} u_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) u_i(\mathbf{r}) + \int d\mathbf{r} \rho(\mathbf{r}) v_{ext}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}^{OEP}[\{u_i\}]. \quad (4)$$

We make use of the chain rule for functional derivatives to obtain from Eq. (3)

$$v_{xc}^{OEP}(\mathbf{r}, [\rho]) = \sum_{i=1}^{occ} \int d\mathbf{r}' \frac{\delta E_{xc}^{OEP}[\{u_i\}]}{\delta u_i(\mathbf{r}')} \frac{\delta u_i(\mathbf{r}')}{\delta \rho(\mathbf{r})} + c.c. \quad (5)$$

where formally $\{u_i[\rho]\}$ are the orbitals which are, however, implicit functionals of the density. Applying the functional chain rule again and after some algebra one obtains the following integral equation:

$$\sum_{i=1}^{occ} u_i(\mathbf{r}) \int d\mathbf{r}' [v_{xc}(\mathbf{r}') - v_i(\mathbf{r}')] G_{si}(\mathbf{r}, \mathbf{r}') u_i^*(\mathbf{r}') + c.c. = 0 \quad (6)$$

where

$$v_i(\mathbf{r}) = \frac{1}{u_i^*(\mathbf{r})} \frac{\delta E_{xc}^{OEP}[u_i]}{u_i(\mathbf{r})} \quad (7)$$

and

$$G_{si}(\mathbf{r}, \mathbf{r}') = \sum_{k \neq i}^{\infty} \frac{u_k(\mathbf{r}) u_k^*(\mathbf{r}')}{\epsilon_i - \epsilon_k}. \quad (8)$$

The integral in Eq. (6) is the fundamental expression for v_{xc} in OEP and can be shown to be equivalent to Eq. (3) [4]. There is no known analytic solution for $v_{xc}[\{u_i\}]$. Therefore, only numerical solutions are

available for spherical atoms [1,4,7,29,30] and for solids [9,13,14] using atomiclike wave functions and assuming integer atomic occupation numbers within each muffin-tin sphere (linear augmented plane-wave method) [11]. These numerical solutions of Eq. (6) are confined to the exchange-only OEP and correlation has been taken into account only via approximate local functionals [9]. In the work of Krieger and co-workers the OEP integral equation is analyzed and a simple approximation is made which reduces the complexity of the original OEP equation significantly and at the same time keeps many of the essential properties of OEP unchanged [7]. Krieger, Li and Iafate gave an exact expression transforming the OEP integral equation (6) into a manageable form. They obtained the following, still *exact* expression for $v_{xc}(\mathbf{r})$:

$$v_{xc}^{OEP}(\mathbf{r}) = v_{xc}^S(\mathbf{r}) + \sum_{i=1}^{occ-1} \frac{\rho_i(\mathbf{r})}{\rho(\mathbf{r})} (\bar{v}_{xci}^{OEP} - \bar{v}_i) + \frac{1}{2} \sum_{i=1}^{occ} \frac{\nabla[p_i(\mathbf{r})\nabla u_i(\mathbf{r})]}{\rho(\mathbf{r})}, \quad (9)$$

$$\bar{v}_i = \int d\mathbf{r} \rho_i(\mathbf{r}) v_i(\mathbf{r}),$$

where $m = occ$ is the highest occupied one electron energy level. $\rho_i = |u_i|^2$ is the partial density. $v_x^S(\mathbf{r})$ is the Slater's potential (its correlation part is not known exactly)

$$v_x^S(\mathbf{r}) = \frac{1}{2\rho(\mathbf{r})} \int d\mathbf{r}' \frac{|\gamma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}, \quad (10)$$

where $\gamma(\mathbf{r}, \mathbf{r}')$ is the first-order density matrix. The summation runs over the orbital index for all the occupied orbitals up to the highest occupied m th orbital (Fermi level). The function p_i is defined by

$$p_i(\mathbf{r}) = \frac{1}{u_i(\mathbf{r})} \int d\mathbf{r}' [v_{xc}^{OEP}(\mathbf{r}') - v_i(\mathbf{r}')] G_{si}(\mathbf{r}, \mathbf{r}') u_i(\mathbf{r}'). \quad (11)$$

In practical applications the last term in Eq. (9) turned out to be quite small in atomic systems and has small effect only on the atomic shell boundaries [7]. This additional term's average over the m th orbitals is zero [7]. Neglecting this term one obtains the exchange-only KLI-approximation which, after some algebra, can be written in the following form [7]

$$v_x^{KLI}(\mathbf{r}) = v_x^S(\mathbf{r}) + \sum_{i=1}^{occ-1} \frac{|u_i(\mathbf{r})|^2}{\rho(\mathbf{r})} \sum_{j=1}^{occ-1} (\mathbf{A}^{-1})_{ij} (\bar{v}_{xj}^S - \bar{v}_{xj}). \quad (12)$$

$$\mathbf{A}_{ji} = \delta_{ji} - \mathbf{M}_{ji}, \quad (13)$$

$$\mathbf{M}_{ji} = \int \frac{\rho_j(\mathbf{r})\rho_i(\mathbf{r})}{\rho(\mathbf{r})} d\mathbf{r}, \quad i, j = 1, \dots, m-1. \quad (14)$$

\bar{v}_{xj}^S and \bar{v}_{xj}^{HF} can be given as follows:

$$\bar{v}_{xj}^S = \int \rho_j(\mathbf{r}) v_x^S(\mathbf{r}) d\mathbf{r}. \quad (15)$$

$$\bar{v}_{xj} = -\frac{1}{2} \sum_{i=1}^{occ} \int d\mathbf{r} d\mathbf{r}' \frac{u_i^*(\mathbf{r}) u_j^*(\mathbf{r}') u_i(\mathbf{r}') u_j(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}, \quad (16)$$

Atomic calculations [8] show that in all situations, the KLI potential mimics the OEP results extremely well and even correctly preserves the property of integer discontinuity [4,11]. Moreover, the KLI method is also easy to program. In this article we restrict ourself to various exchange-only methods, however, the extension of these methods to exchange-correlation case is straightforward using the best available correlation energy functional.

For the constants $w_i = \bar{v}_{xi}^{OEP} - \bar{v}_i$ (Eq. (9)) an alternative expression is proposed by Gritsenko *et al.* [19] in terms of orbital energies ϵ_i . It follows from gauge invariance requirements, proper scaling and short range behaviour of the response part of Eq. (13) that w_j can only depend on an energy difference. In their work Eq. (13) is approximated by:

$$v_x^{SSP}(\mathbf{r}) = v_x^S(\mathbf{r}) + \frac{8\sqrt{2}}{3\pi^2} \sum_{i=1}^{occ-1} \frac{|u_i(\mathbf{r})|^2}{\rho(\mathbf{r})} \sqrt{\epsilon_F - \epsilon_i} \quad (17)$$

We use the notation SSP (Slater's potential + step potential) for this exchange potential. The parameter $\frac{8\sqrt{2}}{3\pi^2}$ is determined from the homogeneous electron gas (HEG) model and therefore Eq. (17) is exact in the HEG limit [19]. This constant is chosen as universal parameter for all the calculations. The main advantage of this expression is that one can avoid the matrix inversion of Eq. (12). Note that the summation runs over all the occupied orbitals except the highest one like in Eq. (12). With the step potential-like second term v_x^{SSP} provides a good approximation to the OEP exchange-potential [19].

In actual calculations we used the following iterative scheme for getting v_x^{KLI} instead of Eq. (12) in each k th SCF cycle

$$v_x^{KLI(k+1)}(\mathbf{r}) = v_x^{S(k)}(\mathbf{r}) + \sum_{i=1}^{m-1} \frac{\rho_i^k}{\rho^k} (\bar{v}_x^{KLI(k)} - \bar{v}_i^k). \quad (18)$$

The initial guess for Eq. (18) is chosen as follows

$$v_x^{KLI(0)}(\mathbf{r}) = \frac{1}{2} (v_x^{LDA}(\mathbf{r}) + 2v_x^S(\mathbf{r})). \quad (19)$$

We found this particular form of the initial guess is close to the KLI exchange potential.

The KLI approximation to OEP provides a self-interaction free exchange potential and proper $-\frac{1}{r}$ asymptotics as $r \rightarrow \infty$. The approximate potentials v_x^S and v_x^{SSP} exhibit proper asymptotics as well [19]. LDA or GGA exchange potentials do not show the correct asymptotic behaviour [7]. For instance, while the popular GGA exchange-correlation energy functional [21] provides energies for atoms with nice agreement with the exact results, the exchange-correlation potentials and the energy eigenvalues of the highest occupied state, are both suffering from error [6,7]. Nevertheless, various forms of GGAs are of great importance and further developments can certainly be expected in this field in the next future [39].

3. Computational details

Closed shell exchange-only KLI calculations have been performed for polyethylene and the results are compared with those from the Hartree-Fock and Slater approach. For all the calculations a new code is used which has been developed in our laboratory [33]. The various one and two-electronic integrals are taken from the Erlangen periodic Hartree-Fock program [32]. During the calculations the number of k -points is set to 25. The SCF iterations are continued until the density matrix elements changed by less than 10^{-5} . 876 and 778 grid points are used for heavy atoms and for hydrogen in the numerical integration using Becke's fuzzy cell method [45]. Thus the total number of grid points per unit cell is 2432. Further computational details of our implementation of polymeric calculations are given elsewhere [15]. For polyethylene the experimental "zig-zag" geometry is used [26]. Since the various properties of polyethylene depend significantly on the geometry, we give the structure we have used for our calculations: the C-C and C-H bond lengths are set to 1.54 and 1.10Å while for the CCC, HCH and HCC angles 113, 108 and 113 degrees are used. Recent geometry optimization calculations with various DFT functionals provided values in very nice agreement with these experimental bonding parameters [35]. Two types of bases are used: the Clementi's minimal (7S/3P) and the larger double- ζ (9S/5P) basis sets for carbon and the 4S and 6S for hydrogen atom, respectively [36]. The (11S/7P) basis set is also employed in certain cases. To make comparison with previously published atomic and molecular results [8,12] and also to check the reliability of our code we have made calculations in the atomic and molecular limit. To do so, we set the translation vector to roughly 20.0 a.u. and choose the interaction only between the nearest-neighbour CH_2 unit cells [24]. Using these parameters the computed properties must be very close to those obtained by atomic or molecular codes. The test provides nice agreement with atomic calculations ob-

tained by Hartree-Fock, Slater's, KLI or SSP exchange-only method which confirms the reliability of our code. Further computational details of our implementation of KLI for polymers are given elsewhere [15].

4. Results

The comparison is carried out for Be, LiH and for N_2 [12,19] in the molecular limit and the energetical results are summarized in Table I. For the total energy we obtained -14.569 , -14.562 , -14.568 a.u. for Be using HF, Slater and KLI methods (with Clementi's minimal basis set). The deviation from HF can be compared with results obtained by others [19]: 7 and 1 mHartree for Slater and KLI, while Gritsenko *et al.* obtained 11 and 0.0, respectively. For LiH the corresponding numbers are: -7.9543 , -7.9542 , -7.9542 a.u. The deviations: 0.0, 0.0 mH, while Grabo *et al.* [12] found 6 mH for Slater. The discrepancy between our and other results can be considered rather small and is probably due to the different basis set applied here. For LiH the highest occupied orbital energies are as follows: $-.2914$, $-.3228$ and $-.3227$ a.u. which are compared with Grabo's values [12], $-.3017$ (HF), $-.3150$ (Slater) and $-.3011$ (KLI). Finally we give the test of our code for H_2 as well. For two-electronic systems the results obtained by HF or KLI must be identical [12]. For E_{tot} and ϵ_m (total energy and highest occupied energy level) the values -1.12796 , -1.127953 and $-.5948$, $-.5913$ a.u. are obtained by HF and KLI, respectively. The small difference must be attributed to numerical inaccuracy in the numerical integration (KLI). Results are also given for N_2 in Table I. The KLI total energy for N_2 differs from the HF one by 9 mH which is comparable with that obtained by a fully-numerical basis-set-free code [12].

Our results for some physical properties of polyethylene are shown in Tables II-III. The results are listed in terms of the order of the neighbouring interaction. Actually, it turns out that at least 5 neighbours are necessary in order to get convergent results for all the physical properties we are interested in within the finite neighbouring approach [15]. For comparison we have calculated all the properties at higher number of neighbouring cells [15].

Our calculation using the large (11S/7P) basis set provides a deeper Hartree-Fock total energy (-39.02326 a.u.) than the one obtained by Suhai [44] using the 6-31G* basis set (-39.02251 a.u.). According to the expectations the comparison of total energies shows us that Hartree-Fock provides the deepest energies while the various Kohn-Sham schemes result in somewhat higher energies. In principle the total energy is always lower in HF than in (exchange-only) OEP since the use of a local potential imposes one more variational constraint on the orbitals [4]. In general, the following inequality holds:

$E_{HF} < E_{OEP} < E_{KLI} < E_{LDA}$ [18]. KLI is always an upper bound to OEP and always lower than E_{LSDX} (local exchange-only spin-density theory). The difference is around 10 mH for KLI. For molecules T. Grabo and E. K. U. Gross [12] found differences around 7-8 mH for KLI. For a larger basis set KLI and HF total energies differ from each other more significantly (23 mH), which is much smaller, however, than the corresponding difference for Slater (44 mH). We believe that the bulk part of the difference is not due to the approximate nature of the exchange potentials applied here, but to the different nature of Hartree-Fock and DFT approaches in accordance with earlier studies [7,12]. These results must be compared with the values obtained by calculations in the molecular limit [12]. Treating the CH_2 unit cell in the molecular limit (Table I), one can see that all the properties (total energy, one electron energies) are close to the Hartree-Fock values. However, in polymer calculations we got for the one electron energies quite significant deviation from the Hartree-Fock values (Tables II-III): employment of local exchange potentials generally leads to higher Fermi level and and at the same time to lower first virtual levels. Therefore, the single particle band gap of polyethylene is smaller for the KS methods than for HF.

We also observe the peculiar behaviour of the highest occupied orbital energies ϵ_m obtained by KLI, which differ from HF values significantly and are closer to $\epsilon_m^{X\alpha}$ [15]. This latter result is rather surprising since atomic and molecular calculations show that the ϵ_m values are very close to those obtained by HF or OEP [7,8,12]. Also, in HF we found no big difference between the highest occupied orbital energy in the molecular limit and in the infinite system. While this comes as a surprise we attribute the increase of the Fermi level due to periodic effects, which come into play only, when one employs localized exchange-potentials for infinite systems. One can follow how the periodic effect comes into play when the change of ϵ_m is examined in terms of the order of the neighbouring interaction in Table II-III. As may be read from Table II-III., when $neig = 1$, ϵ_m obtained by Slater or KLI is the lowest one, however, when $neig$ increased the Fermi level is getting closer to zero progressively. Hartree-Fock does not produce such a phenomenon since it has a *non-local* orbital dependent exchange-potential, which is always deeper than the local counterpart, and thus is keeping the Fermi level at a deeper energy level. However, using the largest basis set in this study (11S/7P) we obtained somewhat higher ϵ_m^{HF} (Table III) as well. As may be seen from Table III, by increasing the number of neighbours and the basis set ϵ_m^{KLI} moves upward significantly and becomes higher than the corresponding LDA value of -0.242 a.u. [15], except for SSP. As can be seen in Tables III, increasing the basis set reduces the calculated KS gap for all the methods, which is mainly due to the lowering of the first virtual level ϵ_{m+1} and to the upward

movement of ϵ_m . While the HF single-particle gap is still too wide (16.6 eV), the calculated Slater's and KLI eigenvalue gaps are too narrow (3.4 and 5.1 eV). Others reported the value of 16.7 eV for the HF gap quite close to our value [40]. It is worth to note, however, that other calculations with 6-31G** basis set resulted in the smaller 13.4 eV for the HF gap [44]. Recent reports proved that the band gap strongly depends not only on the basis set but also on the quality of the finite neighbour approach [40].

It is known [42] that the exact exchange-correlation potential exhibits a discontinuous jump as the number of electrons passes through an integer. This derivative discontinuity plays an important role in the calculations of the exact band gap which can be written as

$$\begin{aligned} \Delta &= \Delta_{nonint}^{KS} + \Delta_{xc} \\ &= \epsilon_{N+1}^{KS}(N) - \epsilon_N^{KS}(N) + \Delta_{xc} \end{aligned} \quad (20)$$

where N is the number of electrons, Δ_{KS}^{nonint} is the Kohn-Sham band gap and Δ_{xc} is the derivative discontinuity. For continuum approximations like LDA or GGA this discontinuity vanishes. However, in OEP as well as in our (orbital-dependent) approximations to OEP, the discontinuity is finite [4,15,22]. The exchange-only contribution to the band gap, Δ_x , is given by [9,22]

$$\begin{aligned} \Delta_x(i \rightarrow \nu) &= \langle u_\nu | \hat{v}_x^{HF} - \hat{v}_x^{OEP}[\rho] | u_\nu \rangle \\ &\quad - \langle u_i | \hat{v}_x^{HF} - \hat{v}_x^{OEP}[\rho] | u_i \rangle \\ &\quad - \langle \nu i | \nu i \rangle - 2 \langle \nu i | i \nu \rangle, \end{aligned} \quad (21)$$

with \hat{v}_x^{HF} being the nonlocal HF exchange operator, however, constructed from the $N/2$ occupied KS orbitals. In our previous study [15] we have calculated Δ_x using Slater and SSP methods and the results can also be seen in Table II-III. The last two terms on the r.h.s. of Eq. (20) will vanish for systems with periodic boundary conditions and an infinite number of unit cells [9]. Since we only take a finite number of cells into account, we will also get contributions to Δ_x from these terms. We have studied the convergence of Δ_x and, for a given basis set, at $neig = 5$ the discontinuity seems to be poorly converged with respect to the basis set and the results have to be read with due caution. In principle the discontinuity is guaranteed to be smaller than the true band gap by its definition [4]. However, calculations do not confirm this expectation for semiconductors [9]. Nevertheless, Δ_x brings the KS gap somewhat closer to the HF one. With the minimal basis set Δ_x represents a rather small correction to the band gap and actually is negative (Table II). This is in contrast with the finding that Δ_x amounts to typically twice the band gap [9]. However, the situation changes completely when a larger basis set is used (Table III). The corrected band gap obtained by the larger basis set with the KLI method (Table III) is 12.8 eV while the Slater and SSP approach yield 9.7 and 12.7 eV, respectively [15].

The much more involved second-order self-energy calculations resulted in 10.3 eV for the quasi-particle (QP) band gap [24,44]. Further corrections to Δ would certainly result in a gap close to the QP and experimental values. According to the expectations KLI and SSP provide values not far from the HF one while the naked Slater potential yields somewhat higher band gap than the experimental value of 8.8 eV [24,38]. In the basis set limit one expects the KLI gap to be close to the HF value. The discrepancy between the KLI gap and the experimental one must be partly attributed to the correlation contribution to the derivative discontinuity (Δ_c). It is also useful to make comparison with quasi-particle calculations where one corrects the HF single-particle gap to get the quasi-particle band structure [24,40,44]. According to the results of Suhai obtained for polyethylene [44] the QP correction reduced the HF gap from 15.0 eV to 10.3 eV while the derivative discontinuity correction raises the OEP gap from 5.1 eV up to 12.8 eV. It would be rather interesting to add on further corrections to Δ_x including correlation at second order level of theory [22]. However, these kind of calculations are beyond the scope of the present article.

Atomic calculations provided KLI eigenvalues which are very close to the HF and OEP values [8]. In molecules, however, Grabo *et al.* found slight deviations from the HF values [12]. Approximate OEP calculations on polyethylene also resulted in eigenvalues different from HF [15]. In Table II-III we have already demonstrated that this is true in the KLI approach as well. In order to make a more detailed analysis of this problem we give the one-electron energies obtained by HF and KLI exchange-only methods in Table IV. We compare the HF and KLI eigenvalues obtained in the molecular limit and in the polymer. In general HF provides deeper eigenvalues by 100 to 200 mH for the core orbitals and much less difference for the valence orbitals. The reverse is true for the KLI virtual orbital energies. The KLI ϵ_m value of -0.093 eV is compared with the values of -0.379 and -0.242 eV obtained by HF and LDA [15], respectively. To sum up, the KLI eigenvalues shift upward in the valence region and shift downward in the virtual space when compared with the HF values in the polymer. The KLI highest occupied orbital energy is rather close to the HF one in the molecular limit. The differences are around 15 and 100 mH, in the molecule and in the polymer.

The exchange energies are also presented for various methods. KLI produces a higher exchange energy than HF by some 30 mH. The reason for this has to be found in the different form of the virial theorem which holds for HF and for DFT. In DFT the virial theorem is as follows [37],

$$E_x[\rho] = \int d\mathbf{r} [3\rho(\mathbf{r}) + \mathbf{r}\nabla\rho(\mathbf{r})]v_x(\mathbf{r}), \quad (22)$$

On the basis of Eq. (22) deeper exchange-potential will

provide deeper exchange energy for the same density. Among the model potentials employed in this study the Slater potential exhibits the deepest potential curve in atoms [7,11] and in Table III one can see that the exchange energy E_x^{Slater} is the deepest and differ from Hartree-Fock by some 50 mH. KLI provides exchange potential similar to that of LDA [19,11] in magnitude, although the shape of the curves are different (see e.g. in refs. [7,11]). The Fermi level ϵ_m is deepest for the Slater's potential among the KS-based methods due to the deepest exchange potential. Even the first virtual level dropped below zero as obtained by the largest basis set by the Slater's exchange potential. The exchange energy obtained by this potential is approximately by 1% lower than the Hartree-Fock exchange energy. This difference is around the magnitude of the non-dynamical correlation energy [16]. Therefore the Slater's potential is a suitable candidate for further calculations together with the commonly used correlation energy functionals which account for only the short range type dynamical correlation energy. The success of the popular exchange energy functionals, such as the one of Becke [45] and the GGA's [21] lie in the overestimation of Hartree-Fock exchange and therefore in the effective treatment of exchange-correlation mainly due to the cancellation of errors with opposite signs [16]. On the basis of Table III v_x^{SSP} provides the best agreement either with the Hartree-Fock total energy or with the exchange energy. Therefore one might speculate that the SSP potential is somewhat closer to the exact OEP potential than to the KLI potential. The v_x^{SSP} is the functional not only of the orbitals but also of the eigenvalues of the KS problem while v_x^{KLI} is only of the orbitals. Further steps in this direction can be desirable in the future in developing a general and accurate potential $v_{xc}^{OEP}\{\{u_i, \epsilon_i\}\}$ [6] which is a functional of the eigensolutions of the KS problem.

In Fig. 1 the band structure is plotted obtained by various methods using the Clementi's double- ζ basis. One can see that virtual bands are appearing below the zero energy level obtained only by the Slater potential. Note that the first three curves in both of the figures are the occupied valence energy levels (Fig. 1 and 2, respectively, the lowest, core level is not plotted). We also note from Fig. 1 that the highest three virtual levels are similar to the virtuals obtained by the minimal basis set (see Fig. 1 in ref. [15]). However, new patterns appear for the first two virtual levels as obtained by the larger basis set (plotted with dashed lines on Fig. 1). The lowest transition from the Fermi level to the first virtual is appearing at the edge of the Brillouin zone ($k = 1$). However, around $k = 0.5$ one can see quasi-degeneracy of certain bands or even crossing of virtual levels close to the edge of the Brillouin zone.

The maximum of the valence band is appearing in the range of $[-2, -11]$ eV with the lowest and highest values

for KLI and Hartree-Fock, respectively, compared to the experimentally suggested values of ionization potential of 9.6 – 9.8 eV [38]. Others give lower experimental values in the 7.6 – 8.8 eV range [24,25]. KLI provides the much lower 2.3 eV value while Slater and SSP give 7.6 and 4.4 eV [15], respectively. By density functional linear muffin-tin orbital method the value of 5.1 eV is obtained for helical polyethylene [25]. The calculated lowest valence band widths for $X\alpha$, HF, SSP, Slater’s and KLI approach are 6.2, 9.0, 4.0, 3.6 and 3.9 eV respectively, which are to be compared with the experimental 7.2 eV [38]. The total valence bandwidths are 14.0 eV ($X\alpha$), 15.4 eV (SSP), 15.6 eV (KLI) and 19.8 eV (HF), compared to a experimental value of 16.2 eV [38]. Slater, KLI and SSP perform quite well for this band width. The calculated gap between the lowest valence band and the minimum of the higher valence bands is 3.3 eV (HF), 1.9 eV ($X\alpha$), 3.0 (SSP), 3.2 (Slater) [15] and 2.8 eV (KLI) compared with the experimental 2.0 eV [38]. The HF and $X\alpha$ values are in accordance with those obtained by others [24,26]. The bottom of the valence band with σ symmetry is 18.0 eV obtained by KLI which is compared with the HF (31.0 eV) and Slater (23.6) eV values. The overall conclusion can be drawn that the various orbital dependent potentials provide band structures similar to one another and all of them differ from HF. The largest deviation from experiment is found for the lowest valence band width (LVBW) which is rather narrow in the OEP methods. HF give too wide LVBW while $X\alpha$ -LDA yields a value in closest agreement with experiment.

Conclusions

Density functionals of the third generation treat both the kinetic and exchange energy exactly at the orbital dependent level of the theory. These orbitals come from a local potential and, due to the Hohenberg-Kohn theorem, are therefore functionals of the density. The optimized effective potential method, in the form given by Talman and Shadwick [1] allows one to treat orbital-dependent functionals in the framework of Kohn-Sham density functional theory. The OEP integral equations are difficult to solve for extended systems and therefore several approximations are introduced. Among them the one obtained by Krieger *et al.* (KLI) and another one derived by Gritsenko *et al.* have become known in the last few years.

In this work we have applied the exchange-only KLI approximation to the OEP approach for insulating polymers. Calculations have been carried out for polyethylene with a new polymer code using the efficient KLI approximation to OEP. The results obtained by the “naked” Slater’s potential and KLI are compared with

those obtained by Hartree-Fock. The addition of the step-potential as a response part of the exact exchange (Eq. 13) to the Slater’s potential considerably improves the quality of various physical properties calculated for polyethylene. To test the quality and reliability of our code we performed calculations in the atomic and molecular limit. The results can be brought into harmony with those obtained by others.

In general, we find that the band structure calculated by different v_x are similar with little qualitative difference, while all of them differ significantly from HF which have valence bands much deeper and much higher virtual levels. The single-particle band gap obtained by the KLI or Slater approaches is too narrow when compared with the experiment. The shifted values are observed for the Fermi level, which differ from Hartree-Fock values significantly. The one electron energy levels are carefully examined and an upward shift of eigenvalues observed when compared with those of HF, and also the counter shift of virtual levels. The deviation from the HF eigenvalues is more significant than in molecules or in atoms. In order to make a valuable comparison with Hartree-Fock, LDA and with the experimental gap, correction must be taken into account to the Kohn-Sham eigenvalue gap. The exchange contribution to the derivative discontinuity is calculated by the KLI exchange potential. In this way the KS single particle gap is corrected by a single shot calculation on top of exchange-only OEP. The exchange contribution to the band gap is somewhat less than twice the KS eigenvalue gap. According to the expectations the corrected gap is much closer to the Hartree-Fock value than the KS eigenvalue gap.

Acknowledgments

This work was supported by the Flemish Science Foundation.

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TABLE I. Comparison of our HF and KLI results (Clementi's double zeta basis) using the code DIOGENES [33] with values from the literature.

E_{tot} and ϵ_m are the total energy and the highest occupied orbital energy in a.u.

		HF ^{our}	HF ^{other}	KLI ^{our}	KLI ^{other}
Be	E_{tot}	-14.569	-14.5730 ^a	-14.5684	-14.5723 ^b
	ϵ_m	-0.3089	-0.3093	-.3092	-.3089
LiH	E_{tot}	-7.954	-7.987 ^b	-7.954	-7.987 ^c
		-7.8629 ^d	-7.8620 ^e		
	ϵ_m	-0.2914	-0.3017 ^b	-0.3227	-0.3011 ^c
		-.2870 ^d	-.2857 ^e		
N ₂	E_{tot}	-108.892 ^f	-108.994 ^d	-108.883 ^f	-108.986 ^c
	ϵ_m	-0.6352 ^f	-0.6152 ^c	-0.6659 ^f	-0.6818 ^c
CH ₂	E_{tot}	-38.8650 ^f		-38.8632 ^f	
	ϵ_m	-0.3750 ^f		-0.3595 ^f	

^a [7]

^b [8]

^c [12]

^dwith STO-3G basis

^ewith STO-3G basis using Gaussian94 [43] program package

^f The large 11S/7P basis set is used for N₂ and for CH₂.

Fig. 1 The calculated valence band structure obtained by various exchange-only methods as a function of the dimensionless variable k with $k = 0$ being the zone center and $k = 1$ the zone boundary. The Brillouin zone is that corresponding to a CH₂ unit cell. Solid lines correspond to the occupied levels while the dashed lines to the virtual levels. The two lowest dashed curves of virtual levels are of particular interest (see text). The Clementi's double- ζ basis set is used and 8 neighbours are considered for the CH₂ unit cell.

TABLE II. Calculated properties of polyethylene by various DFT methods using the minimal basis set HF, Slater, SSP and KLI denote the Hartree-Fock, exchange-only method with Slater's potential, Slater's potential with orbital dependent step potential and the KLI exchange-only OEP method. All the properties are in a.u. except the HOMO-LUMO gap which is given in eV. The Clementi's minimal basis set (7S/3P) is used. $Neig$ gives the number of neighbouring cells taken into account. E_{tot} , E_x are the calculated total and exchange energies per CH_2 unit cell. Δ_x is the exchange component of the derivative discontinuity. The calculations are carried out for the CH_2 unit cell.

neig	HF	Slater ^a	SSP ^a	KLI	
1	E_{tot} (a.u.)	-39.03535	-39.01888	-39.02768	-39.02042
	E_x (a.u.)	-5.82128	-5.84774	-5.79080	-5.7713
	ϵ_m (a.u.)	-.6672	-.5634	-.4924	-.3524
	ϵ_{m+1} (a.u.)	.3978	.0074	-.1084	.2228
	gap (eV)	29.0	15.1	16.4	15.7
	Δ_x (eV)		-5.7	-4.4	-3.2
5		-38.88012	-38.86891	-38.87278	-38.86981
		-5.75048	-5.76397	-5.7379	-5.7297
		-.4747	-.3524	-.2312	-.0871
		.3444	-.0433	.1310	.2786
		22.3	8.4	9.9	10.0
			-3.5	-1.9	-1.2
8		-38.88008	-38.86890	-38.87275	-38.86954
		-5.75049	-5.76400	-5.7378	-5.7284
		-.4760	-.3518	-.2318	-.0972
		.3436	-.0425	.1303	.275
		22.3	8.4	9.9	10.1
			-3.5	-1.9	-1.1
	KS gap+ Δ_x		4.9	8.0	9.0

^a [15]

TABLE III. Calculated properties of polyethylene by various DFT methods using the Clementi's double-zeta basis set (9S/5P).

Results with basis (11S/7P) are also given in the bottom of the Table. The sum of the calculated KS eigenvalue gap Δ_{nonint}^{KS} and the exchange derivative discontinuity Δ_x is also given together with the exchange-only LDA and experimental gap (eV). The notations are the same as in Table I.

neig	HF	Slater ^a	SSP ^a	KLI	
5	E_{tot}	-39.01068	-38.96683	-38.99704	-38.99311
	E_x	-5.8783	-5.9368	-5.8841	-5.8405
	ϵ_m	-.4049	-.2951	-.1628	-.1023
	ϵ_{m+1}	.1489	-.1590	-.0007	.0284
	KS gap	15.1	3.7	4.4	3.6
	Δ_x		3.4	3.8	1.9
8	(9S/5P)	-39.01056	-38.96684	-38.99760	-38.99407
		-5.8780	-5.9367	-5.9036	-5.8621
		-.3984	-.2774	-.1130	-.0997
		.1558	-.1655	-.0755	.0322
		15.1	3.7	4.4	3.6
			3.2	3.7	2.4
8	(11S/7P)	-39.02326	-38.99926	-39.01361	-39.00701
		-5.8977	-5.9486	-5.9036	-5.8553
		-.3786	-.2401	-.1130	-.0933
		.2320	-.1151	.0755	.0958
		16.6	3.4	5.1	5.1
			6.3	7.6	7.7
	KS gap+ Δ_x		9.7	12.7	12.8
	LDA				7.6 ^a
	EXP				8.8 ^b

^a [15]

^b [24,38]

TABLE IV. One-electron energies (a.u.) obtained by HF and KLI exchange-only approaches using the Clementi's (11S/7P) basis set and 8 neighbours for polyethylene ($k=1$)

	HF ^{mol}	KLI ^{mol}	HF ^{poly}	KLI ^{poly}
ϵ_1	-11.289	-10.201	-11.219	-9.820
ϵ_2	-.904	-.774	-.800	-.511
ϵ_3	-.587	-.537	-.681	-.401
ϵ_4	-.375	-.359	-.379	-.093
ϵ_5	.056	-.318	.232	.096
ϵ_6	.240	-.058	.232	.109
ϵ_7	.314	-.005	.392	.301
ϵ_8	.518	.192	.719	.527

