Fundamental gap of molecular crystals via constrained Density Functional Theory

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The energy gap of a molecular crystal is one of the most important properties since it determines the crystal charge transport when the material is utilized in electronic devices. This is, however, a quantity difficult to calculate and standard theoretical approaches based on density functional theory (DFT) have proven unable to provide accurate estimates. In fact, besides the well-known band gap problem, DFT completely fails in capturing the fundamental gap renormalization occurring when molecules are packed in a crystal structures. The failure has to be associated to the inability of describing the electronic polarization and the real space localization of the charged states. Here we describe a scheme based on constrained DFT, which can improve upon the shortcomings of standard DFT. The method is applied to the benzene crystal, where we show that accurate results can be achieved for both the band gap and also the energy level alignment.

I. INTRODUCTION

Molecular crystals have attracted a large amount of interest in both basic and applied science.1 Among their most important properties is the fundamental gap $E_{\text{gap}}$, defined as the energy difference between the ionization potential ($I$) and the electron affinity ($A$), i.e. $E_{\text{gap}} = I - A$. Although for molecules in the gas phase $E_{\text{gap}}$ is typically several eV, this is drastically reduced in solids because of the electrostatic polarization of the crystal, the added charge localized on a molecule is screened by the surrounding dielectric crystal, so that $I$ decreases, while $A$ increases. An analogous effect has been also demonstrated experimentally for molecules adsorbed on polarizable substrates.2–5

From the theoretical perspective, the GW approximation of many-body perturbation theory6 has proven quite accurate in computing $E_{\text{gap}}$ and in accounting for strong renormalization effects both near surfaces4,7 and in bulk crystals.8,9,10,11 Unfortunately, GW is still a computationally very expensive method, which can not be routinely applied to crystals with unit cells typically containing several hundreds atoms. In contrast, density functional theory (DFT) may be seen as a much less demanding alternative, with the occupied Kohn-Sham (KS) eigenstates representing a good zero-th order approximation to the real occupied quasi-particles states (see Ref.10 for a detailed discussion about this issue). However, one has to face several problems when calculating $E_{\text{gap}}$ as the difference between the KS lowest unoccupied and highest occupied molecular orbitals (LUMO and HOMO, respectively) energies, $E_{\text{gap}}^{\text{KS}} = \epsilon_{\text{LUMO}}^{\text{KS}} - \epsilon_{\text{HOMO}}^{\text{KS}}$. Firstly, this procedure results in a considerable underestimation of $E_{\text{gap}}$ already for molecules in the gas phase. Secondly, for crystals, $E_{\text{gap}}^{\text{KS}}$ does not capture the renormalization induced by polarization effect.12,13 A fortuitous error cancellation between the gap underestimation and the lack of renormalization may sometimes happen, but this is not generally the case, which makes quantitative predictions for new materials impossible. Corrective approaches are therefore required, based on a detailed understanding of the origin of these shortcomings of DFT.

On the one hand, the underestimation of the fundamental gap is related to the physical interpretation of the KS eigenenergies as excitation energies. In exact DFT, the “ionization potential theorem”14 establishes the mathematical equality between the KS HOMO energy and the negative of the ionization potential, which means that $\epsilon_{\text{HOMO}}^{\text{KS}} = -I$. In contrast, no analogous theorem exists for the KS LUMO energy. This differs from the opposite of the electron affinity by a number equal to the derivative discontinuity, $\Delta_{\text{xc}}$, of the exchange-correlation functional at integer electron occupation.15,16 A quantity which is not known. Therefore, the fundamental gap and the KS gap do not coincide and $E_{\text{gap}} = E_{\text{gap}}^{\text{KS}} + \Delta_{\text{xc}}$. The difference becomes even larger when approximate functionals are used in DFT. In fact one has $E_{\text{gap}} = E_{\text{gap}}^{\text{KS}} + \Delta_{\text{xc}} + \Delta_{\text{s}}$, with $\Delta_{\text{s}}$ determined by the deviation of the approximate DFT energy from the exact linear dependence on the electron number between two consecutive integer occupations.17,15–18 For the local density approximation (LDA) and the generalized gradient approximation (GGA) of the exchange-correlation functional, $\Delta_{\text{xc}}$ spuriously vanishes, but one still has that $\Delta_{\text{s}}$ is not zero.

Nevertheless, for finite-size systems and, in particular, for small molecules in the gas phase, the fundamental gap can be accurately computed with the $\Delta$SCF method by finite-energy difference.19 This, instead, is not true for...
extended systems, such as molecular crystals. In fact, because of the inherent LDA/GGA self-interaction error, leading to an excessive charge delocalization, a charge added to a system is incorrectly spread over the entire system in order to lower its total energy. As a result, the ΔSCF gap is determined by the fractional charge error of the approximate functional ($\Delta_s$) and becomes equal to the KS gap ($\Delta_e$), so that the two share the same error. This is the essence of band gap problem for extended systems in DFT with LDA/GGA.$^{30,32,33}$

In contrast, the gap renormalization problem is related to the nature of the KS energy levels: they do not capture non-local correlation effects, such as the non-local electronic screening, since they are the eigenvalues of an effective single-particle equation with a local and static potential.

A common approach to go around these problems of standard DFT consists in using hybrid functionals within the generalized-KS scheme (gKS) introduced by Seidl et al. $^{34}$ In fact, the derivative discontinuity of the exact functional is expected to be small and the delocalization error is mitigated. $^{35}$ Furthermore, an effective way to describe the fundamental gap renormalization has been recently proposed by Rafailly-Abramson et al. $^{36}$ These authors introduced a novel range-separated hybrid functional, called Screen-RSH, where the short-range part of the exchange functional is treated in a semi-local approximation, while the long-range part is treated in a screened Fock-like manner, appropriate for incorporating the dielectric response of the crystal.

Here we propose an alternative and complementary approach, which is an extension of the ΔSCF method and prevents the added charge from delocalizing over the entire system. As a consequence the computed fundamental gaps do not revert to the KS gaps. The critical observation is that in molecular crystals the hybridization between the various molecular units is very weak, and each of these units are charge-neutral, with the same number of electrons that they would have in the gas-phase. From this perspective, a molecular crystal looks naturally quite similar to a chain of distant atoms. $^{31}$ Therefore, the fundamental gap can be described with finite total energy difference calculations by enforcing the localization of the added charge on a single molecule. This is efficiently achieved with the constrained DFT (CDFT). Notably, the first attempt in this sense was made by Chan and Ceder $^{32}$ in the context of inorganic semiconductors. In their work the added charge was confined inside a volume commensurate with the range of the dielectric screening effects. By studying about 100 different compounds, they have shown that the accuracy of the results rivals with other state-of-the-art approaches, for instance hybrid functionals and GW, while requiring much less computational resources.

In CDFT an appropriate external potential is introduced in the Kohn-Sham equations in order to implement the desired constraint on the charge density. $^{33}$ Importantly, the CDFT approach is fully variational, so that the energy minimum of the constrained functional represents the ground state of the system under that particular constraint. $^{34,35}$ CDFT has been used successfully for problems concerning molecular systems, for instance for describing long-range charge-transfer excitations between molecules. $^{36,37}$ Moreover, in some recent work, $^{38}$ it has been employed for determining the energy level alignment at hybrid organic-inorganic interfaces. The results have been promising, showing that the method can capture image charge and polarization effects.

The goal of the present work consists in providing a well-defined procedure for the calculation of electron affinities, ionization potentials and fundamental energy gaps of molecular crystals by means of CDFT. This is done by considering the prototypical example of the benzene crystal. The paper is organised as follows: we first describe the computational approach and the methods used in the calculations. Then, we present their application and the results. Finally we conclude mentioning some possible directions for further studies and for additional methodological improvements.

## II. COMPUTATIONAL METHODS

Calculations have been performed by using a development version of the DFT package SIESTA,$^{44}$ which includes an implementation of the CDFT method.$^{38}$ Non-conserving Troullier-Martins pseudopotentials have been employed together with a basis set of double-zeta plus polarization quality. In order to compare our results to those obtained by Rafailly-Abramson et al$^{15}$ with GW and the screen-RSH functional, we have used the same unit cell considered in that work. The lattice vectors have been fixed to the experimental values, while the atomic coordinates inside the cells have optimized with the Perdew-Zunger (PZ) parameterization of the LDA.$^{50}$

The benzene crystal has an orthorhombic unit cell containing four molecules and with lattice parameters $a = 7.44$ Å, $b = 9.55$ Å and $c = 6.92$ Å (see Fig. 1). All computed energy differences are converged up to 5 meV with respect to the number of k-points. The CDFT calculations have also been performed with PZ-LDA. In our implementation, the constraint is applied by requiring that the total charge projected onto a given set of basis orbitals is equal to a specified value. We utilize the Löwdin projection scheme,$^{44}$ which has been shown to give more accurate results than other considered schemes.$^{38,45}$

In the ΔSCF method, the HOMO and LUMO energies of an isolated molecule are computed through total-energy differences

\[ \Delta E_{\text{HOMO}} = -I = E(N) - E(N - 1), \]  
\[ \Delta E_{\text{LUMO}} = -A = E(N + 1) - E(N), \]

where $E(N)$ is the energy of the neutral molecule and $E(N - 1)$ and $E(N + 1)$ are the energies of the corresponding cation and anion, respectively. Analogously,
we calculate the HOMO and LUMO energies of molecular crystals by CDFT as
\[ \epsilon_{\text{HOMO}} = E(N) - E_{\text{CDFT}}(N - 1), \]
\[ \epsilon_{\text{LUMO}} = E_{\text{CDFT}}(N + 1) - E(N), \]
where \( E(N) \) is the total energy of the neutral cell and \( E_{\text{CDFT}}(N - 1) \) and \( E_{\text{CDFT}}(N + 1) \) are the total energies of the same cell with an added hole or electron, respectively. In both the cases the additional charge is constrained to just one cell with an added hole or electron, respectively. Note that both \( E_{\text{CDFT}}(N - 1) \) and \( E_{\text{CDFT}}(N + 1) \) are computed via spin-polarized calculations.

The use of Eqs. (3) and (4) implies that one has to perform a calculation for a charged molecule in a periodic cell. However, the electrostatic energy of a periodically repeated system diverges (the total energy is not bound from below). In order to avoid this problem, it is customary to introduce a uniform charged jellium, which exactly neutralizes the net charge in the cell. As first noted by Leslie and Gillan, the energy of the new system then presents an additional contribution, which is equal to the electrostatic energy of a periodically repeated system containing a point charge \( q \) immersed in the background jellium. Such additional contribution is just the Madelung energy, which writes
\[ E_M = -\frac{q^2 v_M}{2\epsilon}, \]
where \( v_M \) is the Madelung potential and \( \epsilon \) is the macroscopic dielectric screening constant of the material (note that we use atomic units here). Since the Madelung energy represents a spurious addition to the system energy introduced by the computational methodology and due to the use of periodic boundary conditions, it must be removed from the calculated DFT total energy. Once this is done, the correct expressions for the HOMO and LUMO energies, Eqs. (3) and (4), read
\[ \epsilon_{\text{HOMO}} = E(N) - [E_{\text{CDFT}}(N - 1) - E_M|_{q=-1}], \]
\[ \epsilon_{\text{LUMO}} = [E_{\text{CDFT}}(N + 1) - E_M|_{q=1}] - E(N). \]

These equations show that the LUMO energy increases after the application of the Madelung correction, while, conversely, the HOMO energy decreases. This means that the corrected fundamental gap results larger than the uncorrected one.

For a cubic cell of lateral dimension, \( L \), the Madelung potential is available from literature and is equal to \( v_M = \alpha/L \) with \( \alpha = 2.8373 \). However, for the orthorhombic benzene unit cell, the Madelung potential \( v_M \) must be explicitly computed by using the Ewald summation:

\[ v_M = \sum_{R_i \neq 0} \text{erfc}(\eta|\mathbf{R}_i|) + \frac{4\pi}{\Omega} \sum_{G_i \neq 0} e^{-\frac{|G_i|^2}{v_M^2}} - \frac{2\eta}{\sqrt{\pi}} \frac{\pi}{\Omega \eta^2}, \]

where the first and second term are sums over all vectors with cell index \( i \neq 0 \) of the direct (\( \{\mathbf{R}_i\} \)) and reciprocal (\( \{\mathbf{G}_i\} \)) lattice. The rate of convergence of both sums is governed by the parameter \( \eta \), which needs to be chosen so that they can be truncated without introducing any sizeable error. This is done by imposing an error tolerance and cutoff for the direct space summation. Once \( v_M \) has been obtained, the Madelung correction in Eq. (5) and, consequently, the corrected HOMO and LUMO energies can be calculated if the dielectric constant \( \epsilon \) is known. The value of \( \epsilon \) can be obtained from experimental data if available, or computed with the Random Phase Approximation. However, we here calculate \( \epsilon \) by applying a finite size scaling approach, similar to that originally considered by Hine et al. in the study of defect formation energies in oxide insulators.

Firstly, we compute the HOMO and LUMO energies, \( \epsilon_{\text{HOMO}}(\Omega) \) and \( \epsilon_{\text{LUMO}}(\Omega) \), for many supercells of different volume \( \Omega \) by using Eqs. (3) and (4), which are now re-written as
\[ \epsilon_{\text{HOMO}}(\Omega) = E(\Omega, N) - E_{\text{CDFT}}(\Omega, N - 1), \]
\[ \epsilon_{\text{LUMO}}(\Omega) = E_{\text{CDFT}}(\Omega, N + 1) - E(\Omega, N), \]

and thus depend explicitly on \( \Omega \). Then, for each supercell we plot \( \epsilon_{\text{HOMO(LUMO)}}(\Omega) \) as a function of Madelung potential \( v_M \) calculated by the Ewald summation. Finally we fit the corrected value of the HOMO (LUMO) energy, \( \epsilon_{\text{HOMO(LUMO)}} \), and the dielectric constant \( \epsilon \) by using the linear equation
\[ \epsilon_{\text{HOMO(LUMO)}}(\Omega) = \epsilon_{\text{HOMO(LUMO)}} + (-)v_M/2\epsilon, \]

which is obtained from Eqs. (6), (7) and Eq. (8) with \( q^2 = 1 \).

The procedure introduced here has several strengths. Firstly, the dielectric constant is obtained without relying on any input from experiments or any theoretical approach other than CDFT. Secondly, we can inspect whether our results for \( \epsilon_{\text{HOMO(LUMO)}}(\Omega) \) versus \( v_M \) deviate from the linear behavior predicted by Eqs. (6) and (7), thus checking the reliability of the Madelung correction for the present problem. In fact, we note that the Madelung correction is expected to be adequate only...
for systems where the charge distribution can be approximated as point-like. In contrast, for systems where this is not true (for instance for charged defects in semiconductors\cite{makov1993}), different extensions of the Madelung correction have been discussed by Makov and Payne\cite{makov1993}, as well as other authors\cite{makov1993, Payne1993, Hine2012}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{HOMO and LUMO energies of gas phase benzene computed for several supercells with different Madelung potential $v_M$. The energies are in Hartree for better display. Decreasing the Madelung potential is equivalent to increasing the supercell volume $\Omega$, as $v_M(\Omega_n) = v_M(\text{unit cell})/n$. The data have been fitted through a straight line with Eq. (11).}
\end{figure}

III. RESULTS

Before investigating the molecular crystal, we evaluate the fundamental gap of the benzene molecule in the gas phase by using the $\Delta$SCF method. In order to explain how the DFT energies calculated by imposing periodic boundary conditions must be corrected for the Madelung contribution, we employ a supercell approach, where a single molecule is put inside a finite-sized box. In particular, here we consider several symmetric orthorhombic boxes of volume $\Omega_n = n^3(abc)$ with $n = 2, \ldots, 10$ and $a$, $b$ and $c$ being the lattice parameters of the benzene crystal unit cell. Then, by following the procedure outlined above, we compute the HOMO and LUMO energies according to Eq. (10). We can visualize directly the CDFT charge density of the added electron/hole and the consequent rearrangement of the charge density of the surrounding environment (Fig. 3). These rearrangements of the charge density computed by CDFT represent the screening of the host crystal and therefore are of central importance for the subsequent evaluation of the fundamental gap. In Fig. 3 we clearly note that the presence of the electron/hole localized on one molecule induces the formation of a large dipole moment on the molecules of the first coordination shell. This effect however becomes already quite small for the second coordination shell and almost negligible for the third, showing that most of the screening happens in the first coordination shells.

Importantly, as pointed out by Hine et al.\cite{Hine2012}, the fitting procedure that we employ permits for the use of very asymmetric supercells constructed as an array of $l \times m \times n$ copies of the unit cell. This has the advantage that we can access a very large range of systems and, therefore, we can collect a large number of data to address the finite-size scaling problem. In contrast, if only symmetric $n \times n \times n$ supercells were considered, as done in our calculations for the gas-phase molecule, just three data points for the HOMO and LUMO energies would be available, since the calculations become computationally unfeasible already for $n = 4$.

The dependence of the HOMO and LUMO energies over the Madelung potential is presented in Fig. 4. As for the gas phase case, we find an almost perfect linear trend for the HOMO and LUMO energies would be fit according to Eqs. (9) and (10). We can visualize directly the CDFT charge density of the added electron/hole and the consequent rearrangement of the charge density of the surrounding environment (Fig. 3). These rearrangements of the charge density computed by CDFT represent the screening of the host crystal and therefore are of central importance for the subsequent evaluation of the fundamental gap. In Fig. 3 we clearly note that the presence of the electron/hole localized on one molecule induces the formation of a large dipole moment on the molecules of the first coordination shell. This effect however becomes already quite small for the second coordination shell and almost negligible for the third, showing that most of the screening happens in the first coordination shells.

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\begin{figure}[h]
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\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{Difference between the charge density of the neutral supercell and of the supercell with one extra hole (left panel) and on one extra electron (right panel) constrained on one molecule. Red (blue) isosurfaces represent positive (negative) values, i.e. charge accumulation (depletion).}
\end{figure}
behavior of $\epsilon_{\text{HOMO}}(\Omega)$ and $\epsilon_{\text{LUMO}}(\Omega)$ against $v_M$, with the absolute value of the correlation coefficient of the fit being equal to about 0.98. This is very close to the maximal value of 1.0 for an exact linear dependence. Such excellent linear behavior also indicates that the dielectric properties of the benzene crystal are isotropic. If this was not the case, then the data obtained for supercells of different shapes would have shown a large spread, and only data for supercells constructed by repeating the same units along a specific crystallographic direction would have been on a straight line. We remark here that our CDFT energies have an uncertainty of about 10-20 meV with our calculation parameters.

After the linear extrapolation of the data of Fig. 4 we find a dielectric constant, $\epsilon$, of 1.98 and 1.92 depending on whether the fit was performed for the HOMO or LUMO energy, respectively. Although these values somewhat underestimate the experimental one for (liquid) benzene, which is 2.28, they are very close to the RPA value of $\approx 2$. By extrapolating the data to an infinite-sized supercell we find $\epsilon_{\text{HOMO}} = -9.56$ eV and $\epsilon_{\text{LUMO}} = -0.28$ eV so that the fundamental gap reduces from that of the gas phase to 9.28 eV. This corresponds to a renormalization of about 2 eV. Therefore, in the considered insulating molecular crystal, CDFT is demonstrated able to capture non-local correlation effects due to the screening properties of the material. Analogous results have been found for molecules physisorbed on metallic surfaces, which shows that CDFT can correctly describe screening for both metallic and insulating materials.

Note that for all the methods used here (DFT KS eigenvalues, $\Delta$SCF and CDFT) the effective vacuum energy for the crystal needs to be removed from the calculated HOMO and LUMO energies in order to obtain the correct level alignment. This is necessary, since one needs to add to the DFT total energy of the charged system the energy to which the added/removed electron is transferred in a hypothetical experimental setup. Such energy is equal to the vacuum potential above the surface of the molecular crystal. We calculate such vacuum potential for the crystal by making a slab of increasing thickness, and evaluating the KS-potential in the vacuum region. The results are displayed in Fig. 5 and show that for the considered system the vacuum potential decreases with increasing the thickness of the slab. Note that this shift in itself is arbitrary and depends on the used DFT code, since the potential of the entire cell is always defined only up to a constant. The only physically meaningful quantities are differences between eigenvalues or total energies with respect to this vacuum energy. In Fig. 5 we therefore also show the shift of the midpoint energy of the KS HOMO-LUMO gap with increasing number of layers, which for this system is essentially identical to the shift of the vacuum energy. This implies that for the crystal calculation the middle of the band gap for all methods needs to be at the same energy as for the gas phase, since its relative position with respect to the vacuum energy does not change.

The frontier energy levels for the benzene molecule in the gas phase and crystal form as obtained by directly looking at the DFT KS eigenvalues and by using $\Delta$SCF and CDFT, are summarized in Fig. 6. As outlined above, for this system the midpoint of the fundamental gap is at the same energy for both the isolated molecule and the crystal. As expected, we find that the KS gap drastically underestimates the fundamental gap for both the single molecule and the crystal. Even for the KS eigenvalues there is an apparent symmetric 0.3 eV renormalization of the KS HOMO and LUMO energies of the crystal compared to the KS HOMO and LUMO energies of the

FIG. 4: HOMO and LUMO energies of the benzene crystal computed for several supercells with different Madelung potential $v_M$. The energies are in Hartree for better display. The data have been fitted through a straight line with Eq. (11).

FIG. 5: Vacuum energy and middle of the KS gap for supercells, which contain slabs constructed by repeating $N$ benzene crystal unit cells along the non-periodic direction (see inset, which displays one of such supercells for $N = 3$). The vacuum energy is obtained from the Hartree potential in the middle of the vacuum region. The middle of the KS gap is calculated as $(\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}})/2$. The lines interpolating the data are guides for eyes and not fitting curves.
molecule. However, this is not due to polarization effects, but it results from the energy dispersion of the KS band structure in the crystal. In fact, the KS HOMO and the LUMO energies of the benzene crystal are the top of the KS valence band and the bottom of the KS conduction band, respectively, both located at the Γ point in the Brillouin zone (see Fig. 7). These bands have a finite width equal to about 0.6 eV, so that their top and bottom turn out to be displaced by about 0.3 around the band centres, which in turn are perfectly aligned with the isolated molecule KS HOMO and LUMO.

Furthermore, Fig. 6 shows that ∆SCF performs well for the single molecule (note that for the gas phase ∆SCF and CDFT are identical). However, when applied to the crystal, the HOMO and LUMO energies turn out to be equal to the KS HOMO and LUMO energies (i.e. the top of the KS valence band and the bottom of the KS conduction band), and therefore ∆SCF drastically underestimates the gap. In contrast, the CDFT HOMO and LUMO energies are symmetrically displaced respectively toward lower and higher energies when compared to the crystal KS values, so that the calculated CDFT gap becomes notably larger than the KS gap (Fig. 6). Most importantly, the CDFT crystal gap shows the expected renormalization when compared to the gas phase gap. Qualitatively correct results are therefore recovered only with CDFT. From a quantitative point of view, the assessment of the results is hindered by the lack of accurate experimental data for the crystal. We can however compare CDFT and GW results and we observe that the CDFT gap is about 1 eV smaller than the GW one. This difference is already present for the gas phase results, while remarkably the size of gap renormalization predicted by the two methods is in quite close quantitative agreement.

Despite the very satisfactory results obtained for the benzene crystal our method has a number of limitations, which are worth mentioning since one may encounter them when extending the procedure to other systems. The first limitation concerns the spatial distribution of the additional charge. In the case of the benzene crystal such charge is almost completely localized on a single molecular unit, but this may not always be the case for other materials. If the inter-molecular hybridization is large, the constraint may not be well defined. As such enforcing localization on just one molecule will lead to a considerable systematic error. In these cases, one will need to develop a scheme for selecting the correct localization radius, which could follow from considerations about the screening length as proposed by Chan and Ceder in their work on inorganic materials. A second consequence of such partial delocalization is that the Madelung corrections might not be always adequate and more advanced corrective schemes might be required. For instance, if one considers long polyacene compounds, where the added charge is likely to spread over the length of the molecule, the basic assumption that the added charge can be approximated as a point-like one will break down. Finally, at a practical level we note that the method as presented here relies on several calculations for supercells of different sizes. Even though the use of asymmetric supercells effectively helps to limit the maximum size needed, CDFT will become computationally quite demanding for systems where already the unit cell contains many atoms.

IV. CONCLUSIONS AND PERSPECTIVES

We have presented a well-defined computational scheme based on CDFT, which allows us the calcula-
The method is that it relies on DFT total energies rather than on the evaluation of KS eigenvalues. As such one can use local and semi-local functionals, which typically provide an accurate evaluation of the total energy.

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