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Discontinuity of the chemical potential in reduced-density-matrix-functional theory

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Abstract – We present a novel method for calculating the fundamental gap. To this end, reduced-density-matrix-functional theory is generalized to fractional particle number. For each fixed particle number, M, the total energy is minimized with respect to the natural orbitals and their occupation numbers. This leads to a function, E_{tot}^M, whose derivative with respect to the particle number has a discontinuity identical to the gap. In contrast to density functional theory, the energy minimum is generally not a stationary point of the total-energy functional. Numerical results, presented for alkali atoms, the LiH molecule, the periodic one-dimensional LiH chain, and solid Ne, are in excellent agreement with CI calculations and/or experimental data.

Introduction. – Reduced-density-matrix-functional theory has recently attracted a lot of attention [1–8]. Functionals of the one-body reduced density matrix (1-RDM) have been used very successfully in the calculation of correlation energies and dissociation curves of small molecules [9]. Given the success of these functionals it is interesting to evaluate their performance in the calculation of other properties. One particularly interesting quantity in this context is the fundamental gap Δ. It is given by the difference between the ionization potential and the electron affinity

$$\Delta = I - A, \qquad (1)$$

where

$$I = E_{\text{tot}}^{N-1} - E_{\text{tot}}^N, \qquad (2)$$

$$A = E_{\text{tot}}^N - E_{\text{tot}}^{N+1}. \qquad (3)$$

Here, E_{tot}^N is the total ground-state energy of the neutral N electron system while $E_{\text{tot}}^{N\pm 1}$ are the ground-state energies of a system with charge ∓ 1. In the chemistry literature (see, *e.g.*, ref. [10]), $\Delta/2$ is usually termed the *absolute hardness* of a chemical species. Here, we use the term *fundamental gap* for both finite and extended systems since the physical concept defined by eq. (1) is the same in both cases. A method to calculate ionization

potentials within reduced-density-matrix-functional theory (RDMFT) has recently been proposed [11].

Within density functional theory (DFT) one can prove [12] that the fundamental gap is exactly given by the orbital-energy difference $\Delta\varepsilon$ between the lowest unoccupied and the highest occupied Kohn-Sham (KS) state plus a number, Δ_{xc}, which amounts to the discontinuity of the exchange-correlation potential upon adding and subtracting a fractional charge with respect to the N-electron system. This discontinuity is zero for LDA and GGA [12]. Consequently, $\Delta\varepsilon$ is the prediction for the gap within these approximations. This prediction, however, deviates strongly from the experimental values underestimating them by typically 30–50%. Moreover, strongly correlated materials, like FeO and CoO are predicted by LSDA to be metals (zero gap) while, experimentally, these materials are anti-ferromagnetic insulators [13]. Within exact-exchange, one of the variants of DFT functionals, the discontinuity Δ_{xc} differs from zero leading to an overestimation of the fundamental gap. The results are very close to those obtained within Hartree-Fock theory [14]. Consequently, the calculation of the fundamental gap within DFT is still an open problem.

In the present article we propose a method for calculating the fundamental gap by exploiting reduced-density-matrix-functional theory. We derive a rigorous formula for

the fundamental gap and give numerical results for finite and extended systems.

The discontinuity of μ in RDMFT. – In RDMFT the one-body reduced density matrix

$$\gamma(\boldsymbol{r}, \boldsymbol{r}') = N \int \mathrm{d}^3 r_2 \ldots \mathrm{d}^3 r_N \Psi^*(\boldsymbol{r}', \boldsymbol{r}_2 \ldots \boldsymbol{r}_N) \Psi(\boldsymbol{r}, \boldsymbol{r}_2 \ldots \boldsymbol{r}_N)$$

$$(4)$$

is used as the fundamental variable. Here, $\Psi(\boldsymbol{r}_1 \ldots \boldsymbol{r}_N)$ is the many-body wave function of the interacting N-electron system. As was shown by Gilbert [15], one can establish a rigorous one-to-one correspondence between the ground-state wave function and the one-body density matrix. Therefore, all ground-state observables are functionals of the 1-RDM. The main advantage of RDMFT compared to DFT is that the kinetic energy as a functional of $\gamma(\boldsymbol{r}, \boldsymbol{r}')$ is known exactly,

$$T[\gamma] = \int \int \mathrm{d}^3 r \, \mathrm{d}^3 r' \delta(\boldsymbol{r} - \boldsymbol{r}') \left(-\frac{\nabla^2}{2} \right) \gamma(\boldsymbol{r}, \boldsymbol{r}'). \quad (5)$$

Hence, writing the total energy in the form

$$E_{\text{tot}}[\gamma] = T[\gamma] + E_{\text{ext}}[\gamma] + E_{\text{H}}[\gamma] + E_{\text{xc}}[\gamma], \quad (6)$$

where $E_{\text{ext}}[\gamma]$ and $E_{\text{H}}[\gamma]$ are the usual external and Hartree energy functionals, respectively, leads to an exchange-correlation energy which, in contrast to DFT, does not contain any kinetic-energy contributions.

A complication within RDMFT is the absence of a Kohn-Sham system: Due to the idempotency of the density matrix of all non-interacting systems it is impossible to reproduce the density matrix of an interacting system since the latter is always non-idempotent. Nevertheless, one can directly minimize the total energy with respect to the density matrix. In practice, this minimization is replaced by a minimization with respect to the natural orbitals φ_j and occupation numbers n_j which are the eigenfunctions and eigenvalues of γ,

$$\int \mathrm{d}^3 r' \gamma(\boldsymbol{r}, \boldsymbol{r}') \varphi_j(\boldsymbol{r}') = n_j \varphi_j(\boldsymbol{r}). \quad (7)$$

In the minimization, a set of boundary conditions for n's and φ's should be considered. For the natural orbitals the only condition is orthonormality. For the occupation numbers there are two conditions which are necessary and sufficient for the ensemble N-representability of the one-body density matrix for integer particle number [16]. They are the particle number conservation $\sum_{j=1}^{\infty} n_j = N$, and the condition $0 \leqslant n_j \leqslant 1$. The orbital orthonormality and the particle number conservation conditions can be implemented via the Lagrange multipliers μ and ε_{ij} and the functional to be minimized reads

$$F[\gamma] = E_{\text{tot}}[\gamma] - \mu \left(\sum_{j=1}^{\infty} n_j - N \right)$$
$$- \sum_{j,k=1}^{\infty} \epsilon_{jk} \left(\int \mathrm{d}^3 r \varphi_j^*(\boldsymbol{r}) \varphi_k(\boldsymbol{r}) - \delta_{jk} \right). \quad (8)$$

The inequality condition $0 \leqslant n_j \leqslant 1$ allows for optimal sets of n's containing the border values zero and/or one. We refer to these states as pinned states. For these states the derivative $\delta F/\delta n_j$ is not equal to zero in the range $[0, 1]$ and one of the two borders, either zero or one, is accepted as the optimal value for n_j. This situation is most evident for non-interacting particles, where E_{tot} is *linear* in all n_j's. The existence of an occupation number which is equal to one means that the particular natural orbital exists in all the determinants with non-zero coefficient in the full CI expansion. This situation is rather exceptional for the exact wave function of a system of interacting particles. However, it is rather the rule than the exception for most of the existing approximate 1-RDM functionals for systems with more than two electrons. These functionals have the tendency to produce occupation numbers equal to one for most of the core states. Consequently, the functional derivative of F with respect to γ does not vanish at the minimum energy. One should mention that there are functionals which do not produce pinned states [17]. In DFT the situation is very different because any density which integrates to the correct particle number is N-representable. Therefore, the functional

$$F[\rho] = E_{\text{tot}}[\rho] - \mu \left(\int \mathrm{d}^3 r \rho(\boldsymbol{r}) - N \right) \quad (9)$$

always has a minimum with $\delta F/\delta \rho = 0$ at the solution point so that $\delta E_{\text{tot}}/\delta \rho(\boldsymbol{r}) = \mu$.

In order to derive a formula for the fundamental gap within RDMFT we extend the definition of the total-energy functional $E_{\text{tot}}[\gamma]$ to systems with fractional particle number M. Such systems can be described as an ensemble consisting of an N and an $N + 1$ particle state for $N \leqslant M \leqslant N + 1$. The resulting ensemble 1-RDM for the fractional particle number $M = N + \eta$ ($N \in \mathbb{N}$, $0 \leqslant \eta \leqslant 1$) is given by

$$\gamma^M(\boldsymbol{r}, \boldsymbol{r}') = (1 - \eta)\gamma^N(\boldsymbol{r}, \boldsymbol{r}') + \eta\gamma^{N+1}(\boldsymbol{r}, \boldsymbol{r}'), \quad (10)$$

and the lowest energy of the ensemble is

$$E_{\text{tot}}^M = (1 - \eta)E_{\text{tot}}^N + \eta E_{\text{tot}}^{N+1}, \quad (11)$$

where E_{tot}^N and E_{tot}^{N+1} are the ground-state energies of the N and $N + 1$ particle system, respectively. It can be shown that, in complete analogy to the case of integer N, the necessary and sufficient conditions for a given γ to be decomposed as in eq. (10) are: $\sum_{j=1}^{\infty} n_j = M$ and $0 \leqslant n_j \leqslant 1$, where n_j are the eigenvalues of γ^M [18].

As one can see in fig. 1, the derivative $\partial E_{\text{tot}}^M/\partial M$ has a discontinuity at the integer particle number N, which by eqs. (1)-(3) is identical to the fundamental gap

$$\Delta = \left. \frac{\partial E_{\text{tot}}^M}{\partial M} \right|_{N+\eta} - \left. \frac{\partial E_{\text{tot}}^M}{\partial M} \right|_{N-\eta}. \quad (12)$$

So far, the derivation followed exactly the steps known from the generalization of DFT to fractional particle
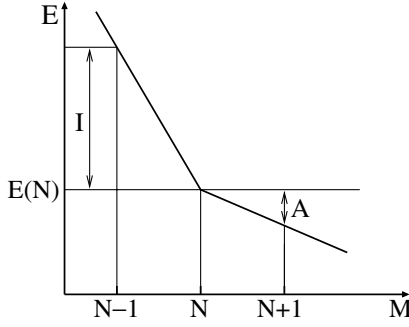
Fig. 1: Total energy for fractional total number of particles.

number [12]. In the following we prove that the Lagrange multiplier, μ, in (8) is identical with the chemical potential, *i.e.*

$$\mu(M) = \frac{\partial E_{\text{tot}}^M}{\partial M}. \qquad (13)$$

In DFT, eq. (13) is a trivial consequence of the variational equation $\delta F/\delta\rho = 0$ which implies that $\delta E_{\text{tot}}/\delta\rho = \mu$ [19]. Consequently, $E_{\text{tot}}^{M+\eta} - E_{\text{tot}}^M = E[\rho^{M+\eta}] - E[\rho^M] = \int \mathrm{d}^3r \times \delta E/\delta\rho(\boldsymbol{r})|_{\rho^M}(\rho^{M+\eta}(\boldsymbol{r}) - \rho^M(\boldsymbol{r})) = \mu(M)\int \mathrm{d}^3r(\rho^{M+\eta}(\boldsymbol{r}) - \rho^M(\boldsymbol{r})) = \mu(M)\,\eta$. In our context of RDMFT however, this equivalence is not at all obvious because $\delta F/\delta\gamma$ need not vanish at the minimum energy (due to the states pinned at the border). To prove (13), we investigate the difference

$$E_{\text{tot}}^{M+\eta} - E_{\text{tot}}^M = E[\gamma^{M+\eta}] - E[\gamma^M] = $$
$$\int\int \mathrm{d}^3r\,\mathrm{d}^3r'\frac{\delta E_{\text{tot}}}{\delta\gamma(\boldsymbol{r},\boldsymbol{r}')}\bigg|_{\gamma^M}\left(\gamma^{M+\eta}(\boldsymbol{r},\boldsymbol{r}') - \gamma^M(\boldsymbol{r},\boldsymbol{r}')\right). \qquad (14)$$

Using the fact that

$$\frac{\delta n_j}{\delta\gamma(\boldsymbol{r},\boldsymbol{r}')} = \varphi_j^*(\boldsymbol{r})\varphi_j(\boldsymbol{r}'), \qquad (15)$$

$$\frac{\delta\varphi_j(\boldsymbol{x})}{\delta\gamma(\boldsymbol{r},\boldsymbol{r}')} = \sum_{\substack{k=1\\k\neq j}}^{\infty}\frac{\varphi_k^*(\boldsymbol{r})\varphi_j(\boldsymbol{r}')}{n_j - n_k}\varphi_k(\boldsymbol{x}), \qquad (16)$$

the functional derivative of (8) yields

$$\frac{\delta F}{\delta\gamma(\boldsymbol{r},\boldsymbol{r}')} = \frac{\delta E_{\text{tot}}}{\delta\gamma(\boldsymbol{r},\boldsymbol{r}')} - \mu\delta(\boldsymbol{r} - \boldsymbol{r}'). \qquad (17)$$

Evaluating $\delta F/\delta\gamma$ via the functional chain rule, (17) leads to

$$\frac{\delta E_{\text{tot}}}{\delta\gamma(\boldsymbol{r},\boldsymbol{r}')} = \mu\delta(\boldsymbol{r} - \boldsymbol{r}') + \sum_j \frac{\delta F}{\delta n_j}\frac{\delta n_j}{\delta\gamma(\boldsymbol{r},\boldsymbol{r}')}$$
$$+ \sum_j \int \mathrm{d}^3x \frac{\delta F}{\delta\varphi_j(\boldsymbol{x})}\frac{\delta\varphi_j(\boldsymbol{x})}{\delta\gamma(\boldsymbol{r},\boldsymbol{r}')} + \text{c.c.} \qquad (18)$$

At the energy minimum, $\delta F/\delta\varphi_j = 0$ and $\delta F/\delta n_l = 0$ for any unpinned state l. The pinned states, however, contribute so that

$$\frac{\delta E_{\text{tot}}}{\delta\gamma(\boldsymbol{r},\boldsymbol{r}')}\bigg|_{\min} = \mu\delta(\boldsymbol{r} - \boldsymbol{r}') + \sum_p \frac{\delta F}{\delta n_p}\varphi_p^*(\boldsymbol{r})\varphi_p(\boldsymbol{r}'), \quad (19)$$

where we have used (15) and the sum runs over those pinned states for which $\delta F/\delta n_p \neq 0$. Equation (14) therefore reduces to

$$E_{\text{tot}}^{M+\eta} - E_{\text{tot}}^M = \mu(M)\eta + \sum_p \frac{\delta F}{\delta n_p^M}$$
$$\times \int\int \mathrm{d}^3r\,\mathrm{d}^3r'\varphi_p^{*M}(\boldsymbol{r})\varphi_p^M(\boldsymbol{r}')\left(\gamma^{M+\eta}(\boldsymbol{r},\boldsymbol{r}') - \gamma^M(\boldsymbol{r},\boldsymbol{r}')\right). \qquad (20)$$

If we write the occupation numbers and orbitals of the $M + \eta$ system as

$$n_j^{M+\eta} = n_j^M + \delta n_j, \quad \varphi_j^{M+\eta} = \varphi_j^M + \delta\varphi_j, \qquad (21)$$

we can obtain the first-order corrections of $\gamma^{M+\eta}$. The changes δn_j and $\delta\varphi_j$ in eq. (21) are not arbitrary. They are the changes in the optimal n_j and φ_j if an infinitesimal charge η is added to the system. Using the orthonormality of the natural orbitals we get

$$E_{\text{tot}}^{M+\eta} - E_{\text{tot}}^M = \mu(M)\eta + \sum_p \frac{\delta F}{\delta n_p^M}$$
$$\times \left[\delta n_p + n_p^M \int \mathrm{d}^3r \left(\varphi_p^M(\boldsymbol{r})\delta\varphi_p^*(\boldsymbol{r}) + \delta\varphi_p(\boldsymbol{r})\varphi_p^{*M}(\boldsymbol{r})\right)\right]. \qquad (22)$$

The second term in the square brackets is zero since the norm of the natural orbitals does not change and the first term is zero because the sum runs only over pinned states and for these $\delta n_p = 0$, *i.e.* no states get unpinned. The states that would most likely get unpinned are those where the "true" energy minimum ($\delta F/\delta n = 0$) lies at a small distance outside the allowed interval. However, this distance is still finite and the infinitesimal additional charge η cannot move the true minimum inside the allowed interval. This completes the proof of (13). Hence, by (12), we can evaluate the fundamental gap from the discontinuity of the Lagrange multiplier $\mu(M)$:

$$\Delta = \lim_{\eta\to0}[\mu(M+\eta) - \mu(M-\eta)]. \qquad (23)$$

Results. – Equation (23) is of course proven for the exact functional. It is interesting to test it using approximate functionals $E[\gamma]$. We employed the functional of Goedecker and Umrigar [3] (GU) which has the same structure as the Müller functional [1,2] with the important difference that the self-interaction terms are explicitly removed. Our implementation for atoms and molecules is based on a Gaussian basis set expansion of the natural
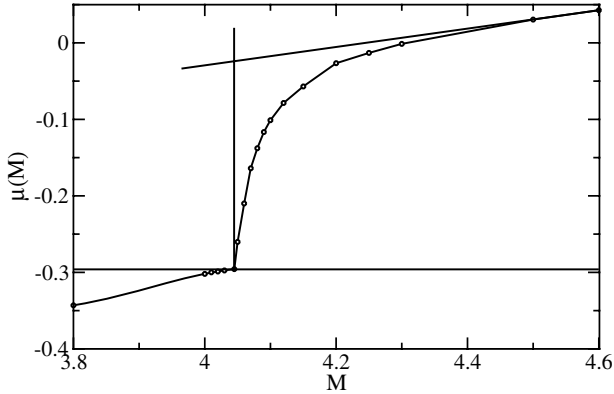
Fig. 2: The chemical potential μ (in hartree) as a function of particle number M for the LiH molecule.

Table 1: The fundamental gap for some atoms and small molecules as well as the LiH chain, and solid Ne from RDMFT compared to other calculations and experimental values; all gaps are given in hartree. ([a])QCI from ref. [22]; ([b])from ref. [23]; ([c])ionization potential from [22], electron affinity from [24]; ([d])CISD using the same basis set as in RDMFT; ([e])ionization potential from ref. [25], electron affinity from [26]; ([f])LDA, with CRYSTAL code [27] and the same basis set; ([g])GGA, with CRYSTAL code [27] and the same basis set; ([h])from ref. [28].

	RDMFT	Other theoretical	Experiment
Li	0.18	0.175([a])	0.175([b])
Na	0.18	0.169([c])	0.169([b])
LiH molecule	0.27	0.286([d])	0.271([e])
LiH chain	0.64	0.500([f]), 0.509([g])	
Ne solid	0.76	0.439([f]), 0.546([g])	0.797([h])

orbitals and uses the GAMESS [20] computer code to calculate the one- and two-electron integrals. We minimize the total energy with respect to both the natural orbitals and the occupation numbers employing a conjugate gradient scheme. Since the N-representability conditions for fractional particle number are identical to those for integer [18], the generalization to fractional particle numbers is straightforward. We obtained the fundamental gap for several small molecules using 20 to 30 natural orbitals which were expanded in a cc-PVQZ atomic Gaussian basis set [21].

Figure 2 shows the result of the numerical calculations for the LiH molecule using the GU functional. There is a step near $M = 4$ which is sharp at the lower edge but relatively smooth at the upper edge. The discontinuity of $\mu(M)$ is located at a value slightly higher than $M = 4$ precisely at the point where the highest fractional occupation number crosses one and gets pinned. These features are due to the approximate nature of the exchange-correlation energy. The exact functional would show the discontinuity exactly at $M = 4$. In order to extract a numerical value for the gap from the graph in fig. 2 we used the intersection of the extrapolated curve $\mu(M)$ for $M > 4$ and a vertical line at the position of the jump.

The results for the fundamental gap of Li, Na, and LiH calculated with the GU functional are given in table 1 and are in very good agreement with state of the art CI calculations. They also agree very well with experimental data. Note that in the context of DFT, these values are exceedingly difficult to calculate because, within standard LDA/GGA-type functionals, the negative ions of such small systems are not even bound.

For periodic systems the symmetry properties of the many-body wave function imply that

$$\gamma(\boldsymbol{r} + \boldsymbol{R}, \boldsymbol{r}' + \boldsymbol{R}) = \gamma(\boldsymbol{r}, \boldsymbol{r}') \qquad (24)$$

for arbitrary lattice vectors $\boldsymbol{R}$. This property, on the other hand, implies that the eigenfunctions of γ, *i.e.* the natural orbitals, are Bloch functions, $\varphi_{\lambda \boldsymbol{k}}(\boldsymbol{r})$, where λ is a band index and $\boldsymbol{k}$ is a wave vector in the first Brillouin zone [29]. Hence, the spectral representation of γ reads

$$\gamma(\boldsymbol{r}, \boldsymbol{r}') = \sum_{\lambda, \boldsymbol{k}} n_{\lambda \boldsymbol{k}} \, \varphi_{\lambda \boldsymbol{k}}^*(\boldsymbol{r}') \, \varphi_{\lambda \boldsymbol{k}}(\boldsymbol{r}) \, . \qquad (25)$$

In principle, one should now minimize the total energy with respect to the occupation numbers $n_{\lambda \boldsymbol{k}}$ and the natural orbitals $\varphi_{\lambda \boldsymbol{k}}(\boldsymbol{r})$ as described above for finite systems. However, with the approximate functionals currently available, we encounter a serious difficulty: For the Müller functional $\mu(M)$ does not show any discontinuity for all the systems we studied so far. The self-interaction correction of Goedecker and Umrigar [3] seems to be essential to reproduce this feature. However, in terms of Bloch orbitals, the self-interaction terms go to zero, *i.e.*, the GU functional reduces to the Müller functional if Bloch orbitals are inserted. To properly subtract the spurious self-interaction one has to use localized orbitals [30,31], such as Wannier functions. Inserting the standard transformation from Bloch to Wannier functions,

$$\varphi_{\lambda, \boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{R}} e^{i \boldsymbol{k} \boldsymbol{R}} \, \omega_{\lambda}(\boldsymbol{r} - \boldsymbol{R}), \qquad (26)$$

in eq. (25), the 1-RDM can be represented as

$$\gamma(\boldsymbol{r}, \boldsymbol{r}') = \sum_{\lambda} \sum_{\boldsymbol{R}, \boldsymbol{R}'} g_{\lambda}(\boldsymbol{R} - \boldsymbol{R}') \, \omega_{\lambda}^*(\boldsymbol{r}' - \boldsymbol{R}') \, \omega_{\lambda}(\boldsymbol{r} - \boldsymbol{R}), \qquad (27)$$

where $\omega_{\lambda}(\boldsymbol{r})$ is the Wannier function referring to band λ and

$$g_{\lambda}(\boldsymbol{R} - \boldsymbol{R}') = \sum_{\boldsymbol{k}} n_{\lambda \boldsymbol{k}} e^{i \boldsymbol{k} (\boldsymbol{R} - \boldsymbol{R}')} \, . \qquad (28)$$

For systems with a gap, the Wannier functions decay exponentially. Hence, we expect that the products $\omega_{\lambda}^*(\boldsymbol{r}' - \boldsymbol{R}') \omega_{\lambda}(\boldsymbol{r} - \boldsymbol{R})$ contribute very little to γ if $\boldsymbol{R} \neq \boldsymbol{R}'$. As a

first implementation we neglect these off-diagonal terms altogether by making the approximation

$$g_\lambda(\boldsymbol{R} - \boldsymbol{R}') = n_\lambda\,\delta(\boldsymbol{R} - \boldsymbol{R}') \qquad (29)$$

which leads to

$$\gamma(\boldsymbol{r}, \boldsymbol{r}') = \sum_{\lambda, \boldsymbol{R}} n_\lambda\,\omega_\lambda^*(\boldsymbol{r}' - \boldsymbol{R})\,\omega_\lambda(\boldsymbol{r} - \boldsymbol{R}). \qquad (30)$$

Restricting the search to density matrices of the form (30), we can then go ahead and minimize the total energy with respect to the Wannier functions and their occupation numbers n_λ using the GU functional. The self-interaction terms, when evaluated with Wannier orbitals, do not vanish and we obtain reasonable results (see below). The restricted search over density matrices of the form (30) can be viewed in yet another way: By eq. (28), the approximation (29) amounts to neglecting the k-dependence of the Bloch occupation numbers, $n_{\lambda k} \approx n_\lambda$. This is expected to be a good approximation for insulators. For metals on the other hand, the approximation breaks down completely because $n_{\lambda k}$ changes, at the Fermi surface, from values close to one to values close to zero within the same band.

We implemented the minimization of the 1-RDM functionals in the space of Wannier states using the Wannier computer code described in [32,33]. As a first test case, we considered a system in one dimension, namely the LiH chain. As in the case of finite systems, $\mu(M)$ shows a pronounced step. The size of this step compares favorably with the LDA and GGA values (see table 1). Clearly, there are no experimental data available for this system but, as always, the LDA/GGA results are expected to be smaller than the true value.

As a first fully three-dimensional system, we performed a calculation for solid Ne. Figure 3 shows the discontinuity of the chemical potential when only the occupation numbers are optimized. The discontinuity in Ne appears slightly above 10 which is again due to the approximate nature of the exchange-correlation functional. The value of the gap, extracted from fig. 3 by extrapolation, is also included in table 1 and compares very well with the experimental value.

In conclusion, we have presented a method to calculate the fundamental gap of finite systems and periodic solids within reduced-density-matrix-functional theory. First numerical results were obtained using a recently proposed 1-RDM functional. For all systems studied, the chemical potential shows a clear discontinuity as a function of the total number of electrons if all self-interaction terms are removed. The extracted gap values agree better with CI calculations and/or the experiment than any standard DFT or Hartree-Fock calculation.
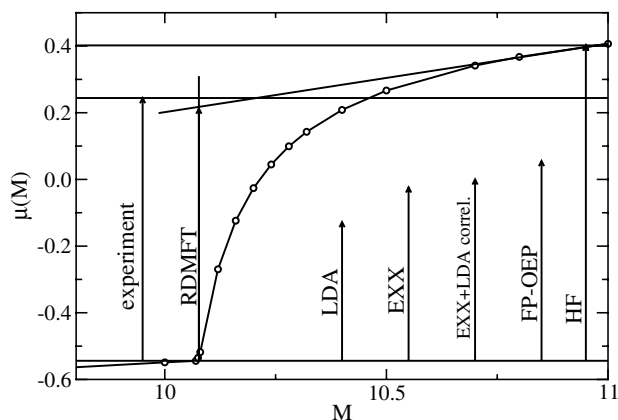
$$* * *$$

Fig. 3: The chemical potential μ (in hartree) as a function of particle number M for solid Ne. The value of the gap is compared with HF, various DFT calculations [34] and with experiment [28].

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