

# The Kohn–Sham gap, the fundamental gap and the optical gap: the physical meaning of occupied and virtual Kohn–Sham orbital energies

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A number of consequences of the presence of the exchange–correlation hole potential in the Kohn–Sham potential are elucidated. One consequence is that the HOMO–LUMO orbital energy difference in the KS-DFT model (the KS gap) is not “underestimated” or even “wrong”, but that it is physically expected to be an approximation to the excitation energy if electrons and holes are close, and numerically proves to be so rather accurately. It is physically not an approximation to the difference between ionization energy and electron affinity  $I - A$  (fundamental gap or chemical hardness) and also numerically differs considerably from this quantity. The KS virtual orbitals do not possess the notorious diffuseness of the Hartree–Fock virtual orbitals, they often describe excited states much more closely as simple orbital transitions. The Hartree–Fock model does yield an approximation to  $I - A$  as the HOMO–LUMO orbital energy difference (in Koopmans’ frozen orbital approximation), if the anion is bound, which is often not the case. We stress the spurious nature of HF LUMOs if the orbital energy is positive. One may prefer Hartree–Fock, or mix Hartree–Fock and (approximate) KS operators to obtain a HOMO–LUMO gap as a Koopmans’ approximation to  $I - A$  (in cases where  $A$  exists). That is a different one-electron model, which exists in its own right. But it is not an “improvement” of the KS model, it necessarily deteriorates the (approximate) excitation energy property of the KS gap in molecules, and deteriorates the good shape of the KS virtual orbitals.

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## 1. Introduction

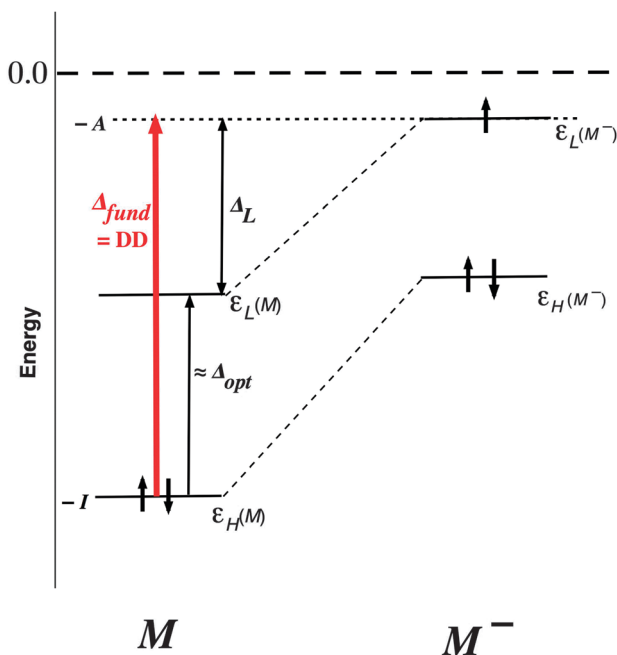
Although the physical meaning of the orbital energies of the Kohn–Sham (KS) molecular orbital model of density functional theory (DFT)<sup>1</sup> has been known for some time, there is still considerable attention and even controversy on this point in the literature.<sup>2–12</sup> Maybe the most striking manifestation of this is the frequent reference to “the band gap problem” of DFT: in particular in the solid state community, but also in the (quantum) chemistry community it is often stressed that the “KS gap is wrong”, namely strongly underestimated. What is meant is that this orbital energy gap is much smaller than what is called the fundamental gap in solid state physics (the difference  $I - A$  between ionization energy and electron affinity) and either the same difference  $I - A$  (twice the chemical hardness) in a molecule, or just the Hartree–Fock HOMO–LUMO gap,

which is the Koopmans frozen orbital approximation to  $I - A$ . It is on the other hand well known that the KS gap is not even in theory close to (let alone equal to) the difference  $I - A$ . If a negative ion is formed by putting an electron in the LUMO, all one-electron levels will shift up, see Fig. 1. Indeed, it is known from the asymptotics of the electron density<sup>13–18</sup> that  $\epsilon_L(M^-) = -I(M^-) = -A(M)$ , where  $M$  and  $M^-$  are a closed shell molecule and its anion and  $I$  and  $A$  denote the (first) ionization energy and the electron affinity, respectively. We note that the analysis of noninteger electron systems by Perdew, Parr, Levy *et al.*<sup>14,19,20</sup> has revealed that immediately upon crossing the integer, *i.e.* in  $N + \delta$  electron systems, an upshift of the LUMO by exactly the amount  $\Delta_L$  has to occur, which is why there should be a spatially constant (at least over the molecular region) upshift of the xc potential  $v_{xc}$ . This constant upshift, usually denoted  $\Delta_{xc}$ , or  $C(J)$ ,<sup>21</sup> and often called the derivative discontinuity, is of course just  $\Delta_L$ . But the quantity  $\Delta_L$  is a property of integer electron systems, and in our discussion here we do not need the fractional electron systems, so we stick to  $\Delta_L$  in order to avoid the confusion that this  $\Delta_L$  “is caused by” the derivative discontinuity jump  $\Delta_{xc}$ . It is the other way around: the analysis by Perdew *et al.* has shown that the derivative

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**Fig. 1** Illustration of the (exact) KS orbital energies of the HOMO and LUMO of the neutral closed shell  $N$ -electron molecule  $M$  ( $H = N/2$ ,  $L = N/2 + 1$ ), and the corresponding levels of the anion  $M^-$ . Quantities are defined in eqn (1).

discontinuity jump must be equal to  $\Delta_L$ . Fig. 1 depicts this well-known state of affairs:

$$\begin{aligned}\varepsilon_H(M) &= -I(M); & \varepsilon_L(M^-) &= -I(M^-) = -A(M) \\ \Delta_L &= \varepsilon_L(M^-) - \varepsilon_L(M) = -A - \varepsilon_L(M) \\ \Delta_{\text{gap}}^{\text{KS}} &= \varepsilon_L(M) - \varepsilon_H(M) \approx \Delta_{\text{opt}} \\ \Delta_{\text{fund}} &= I - A = \varepsilon_L(M^-) - \varepsilon_H(M) = \Delta_{\text{gap}}^{\text{KS}} + \Delta_L\end{aligned}\quad (1)$$

(If a quantity refers to  $M$  we will often omit this; if it refers to  $M^-$  we will always indicate that explicitly.) The fundamental gap is  $\Delta_{\text{fund}} = I - A = \varepsilon_L - \varepsilon_H + \Delta_L = \Delta_{\text{gap}}^{\text{KS}} + \Delta_L$ . The fundamental gap  $\Delta_{\text{fund}}$  is equal to the discontinuity in the derivative of the total energy at the integer point,  $\text{DD} = I - A$ . From the point of view that it is unfortunate that the KS gap and fundamental gap are not equal, and sometimes from the notion that the discontinuity jump in the KS potential is lacking in  $\varepsilon_L(M)$  and “should be incorporated”, attempts are being made to obtain adaptations of the KS model, or alternatives to the KS model, so that the one-electron energies become Hartree–Fock like, *i.e.* approximate  $I - A$  better than the KS model does. We will argue in this contribution that this is not a necessary and maybe even undesirable route. It does not seem to be fully appreciated that the KS model has actually the great advantage that the KS gap is a very good measure for the lowest excitation energy in molecules: it is physically an excitation of the KS system (not an electron addition, as in Hartree–Fock), so it should be a good measure of the optical gap  $\Delta_{\text{opt}}$ , and actually is an excellent approximation to it (in molecules). Historically it has been considered a disadvantage of the Hartree–Fock model that its virtual orbitals exhibit a large upshift, and are very diffuse.

This makes the simple use of the energies and composition of the lowest virtual orbitals for a quick guess of the energies and nature of the lowest excited states much less straightforward with Hartree–Fock than with simple semi-empirical approaches like PPP and (extended) Hückel. The KS orbitals, however, do not suffer from the poor shape (diffuseness) of the HF virtual orbitals (see below). Now that with the KS model we have a more accurate one-electron model, which brings the virtue of easy interpretation of the excitation spectrum back, it is remarkable, and maybe deplorable, that so much effort is put into working one’s way back to a Hartree–Fock like approach.

We comment in this communication first on the occupied orbital energy spectrum (both exact KS and approximate DFT (LDA, GGA)), in relation to the ionization energies, then on the virtual spectrum (Section 3), in relation to excitation energies, with emphasis on the important difference between the nature and shape of Hartree–Fock (and Hartree–Fock–Kohn–Sham or generalized Kohn–Sham) virtual orbitals and Kohn–Sham virtual orbitals. We stress the often unrealistic nature of Hartree–Fock virtual orbitals. Next, some of the properties of density functional approximations (DFA), LDA (local density approximation) and GGA (generalized gradient approximation) are discussed (Section 4), in particular with respect to excitation energies. After some preliminary remarks on the importance of electron–hole interactions in excited states (Section 5) the cases where DFAs do not work well, long range charge transfer excitations (Section 6) and excitations in solids (Section 7) are treated. Finally some comments are made on the Hartree–Fock–Kohn–Sham (generalized Kohn–Sham) schemes.

## 2. Occupied orbital energies, ionization energies, and DF approximations

It is important to distinguish between properties of the *exact* KS model and approximations like LDA and GGA. We use “Kohn–Sham” and “DFT” exclusively for the exact theory; approximations (LDA and GGA) will be explicitly indicated. It is well known that the exact KS model requires an orbital energy for the highest occupied orbital that is equal to the first ionization energy. This was established from the comparison to the long-range asymptotics of the exact electron density  $\rho$  of the system.<sup>13–18</sup> The KS density is governed by the asymptotic decay of the least bound occupied orbital as  $\rho(r) \sim \exp[-2\sqrt{-2\varepsilon_H}]$ , while the exact density is known to decay as  $\rho(r) \sim \exp[-2\sqrt{2I}]$ , from which  $\varepsilon_H = -I$  follows. However, it is still often stated that the other orbital energies have no physical meaning, and that it is a pity that nothing like Koopmans’ theorem to give meaning to the other occupied orbital energies exists. The truth could not be more different: it has been established<sup>22–25</sup> that the KS orbital energies of the valence levels in molecules approximate the experimental ionization energies much more closely (typically at 0.1 eV level) than the Hartree–Fock orbital energies do (difference with IPs typically  $\sim 1$  eV). Table 1 gives an illustration. It should be stressed that this holds for the true KS orbital energies. It is possible to approximate the (unique!) local KS potential

**Table 1** “Koopmans’ theorem” in Kohn–Sham DFT: Hartree–Fock and (exact) KS orbital energies of H<sub>2</sub>O compared to ionization energies.<sup>22</sup> Energies in eV

MO	HF	KS	Expt	$I_k + \varepsilon_k^{\text{KS}}$
Valence	$-\varepsilon_k$	$-\varepsilon_k$	$I_k$	
1b <sub>1</sub>	13.76	12.63	12.62	−0.01
3a <sub>1</sub>	15.77	14.78	14.74	−0.04
1b <sub>2</sub>	19.29	18.46	18.55	0.09
Av. dev.	0.97	0.05		
Lower val. and core				
2a <sub>1</sub>	36.48	30.89	32.2	1.31
1a <sub>1</sub>	559.37	516.96	539.90	22.49

belonging to the exact ground state density very well by taking a very accurate density from large scale CI calculations and reconstructing the KS potential that reproduces this density with KS orbital calculations. Several procedures to achieve this exist.<sup>26–30</sup> We have used the procedure of ref. 27 that exploits the Hohenberg–Kohn inequality  $\int \Delta\rho(\mathbf{r})\Delta v(\mathbf{r}) < 0$ , which is usually invoked to prove that a change  $\Delta v$  in the potential necessarily must imply a change  $\Delta\rho$  in the density (or else one would obtain equality to 0 for the integral). The inequality also implies that when  $\Delta v$  is negative over a small region, the change  $\Delta\rho$  must be positive (on average) over that region in order to obtain  $< 0$ , and *vice versa*. This implies that one can iteratively adjust the external potential ( $v_s$  in the KS system) until it matches the exact density, see applications in ref. 27 and 31–33. When presenting “exact” KS results we always use results obtained in this way.

The excellent correspondence of exact valence KS orbital energies and ionization energies (“Koopmans’ theorem of DFT”),

$$\varepsilon_i^{\text{KS}}(i \in \text{val}) \approx -I_i \quad (2)$$

that is observed in such “exact” (numerical accuracy better than 0.05 eV) KS calculations<sup>22–25</sup> has a very different origin than in the case of Hartree–Fock. It is not related to a frozen orbital approximation for the ion, but since the KS electron system is tied to the exact system and wavefunction, it should come as no surprise to find that the relation between KS orbital energies and ionization energies can be derived from the exact wavefunction rather than from frozen orbital single determinant trial wavefunctions. The photoionization spectrum typically consists of a number of intense main peaks, each with a few close-lying much weaker satellite peaks. Interestingly, the KS orbital energy is a weighted average over such a main peak and the accompanying satellite peaks,<sup>24</sup>

$$\varepsilon_i^{\text{KS}}(i \in \text{val}) = -n_i I_i - \sum_{j \in S(i)} n_j I_j + w_i \quad (3)$$

(the Krieger–Li–Iafrate constants  $w_i$  are small for valence levels). Typically the main peak with ionization energy  $I_i$  has a wavefunction that is well approximated by a single orbital ionization, and the sum over  $j$  (which can be ignored in first approximation) runs over the set of usually much less intense satellites  $S(i)$  of main peak  $i$ . The spectroscopic factors  $n_i$  are related to the intensity of the peaks;  $n_j$  is the norm of the (unnormalized)

Dyson orbital of the corresponding ion state  $\Psi_j^{N-1}$ ,  $d_j(\mathbf{x}_1) = \sqrt{N} \int \Psi_j^{N-1*}(\mathbf{x}_2, \dots, \mathbf{x}_N) \Psi_0^N(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N$ . [The main, intense, peaks in the photoionization spectrum correspond to simple orbital ionizations, *i.e.* the wavefunction is in first approximation close to the Koopmans’ ion state. Satellites are peaks with relatively small intensity near the intense main peak, which “borrow” intensity from the main peak. The corresponding ion states have wavefunctions that are approximately some other orbital ionization than the main peak plus an excitation. The main peak and its satellites are characterized by Dyson orbitals of the corresponding ion states, all having the same shape, but different norms: the main peak has typically  $n_i \approx 1$ , the satellites have norms  $\ll 1$ . The  $n_i$ s are proportional to the intensity of the photoelectron spectrum (it is 1 if there are no satellites). For further details see ref. 24.] Relation (2) is more closely obeyed for MOs with ionizations that have little satellite structure, *i.e.* in particular for outer valence MOs, see Table 1. There are no satellites to the first ionization potential, so (2) turns in the case of the KS HOMO to the exact equality  $\varepsilon_{\text{H}} = -I_{\text{H}}$  depicted in Fig. 1. For the upper valence MOs with generally weak satellites,  $\varepsilon_i^{\text{KS}}$  of the KS solution differs from  $-I_i$  by only *ca.* 0.1 eV.<sup>22–25</sup>

As is well known, the energies  $\varepsilon_i^{\text{HF}}$  of the occupied Hartree–Fock (HF) MOs have the approximate interpretation  $\varepsilon_i^{\text{HF}} \approx -I_i$  by virtue of Koopmans’ theorem<sup>34</sup> based on the frozen-orbital approximation.  $\varepsilon_{\text{H}}^{\text{HF}}$  provides a fair estimate of  $-I_{\text{H}}^{\text{KS}}$ , *cf.* the prototype molecules in Table 3. Indeed, though  $\varepsilon_{\text{H}}^{\text{HF}}$  is lower in all cases (except HCN and FCN) than  $\varepsilon_{\text{H}}^{\text{KS}}$ , the corresponding difference does not exceed 1.5 eV, and in the cases of N<sub>2</sub>, HCN, FCN, and HCl the KS and HF HOMO energies are (unusually) close to each other (See Table 3). This comes from a cancellation of errors in the Hartree–Fock case: the frozen orbital approximation makes the ionization energy too large, but the neglect of correlation is a more severe approximation in the molecule than in the ion, which tends to make the ionization energy too small, see further discussion in Section 3.

The demonstrated proximity of  $\varepsilon_{\text{H}}^{\text{KS}}$  and  $\varepsilon_{\text{H}}^{\text{HF}}$  is not accidental. Electrons in both KS and HF occupied MOs interact with  $(N - 1)$  electrons through the KS potential  $v_s(N - 1) = v_{\text{Coul}}(N) + v_{\text{xc}}(-1)$  and the HF potential  $v_i^{\text{HF}}(N - 1) = v_{\text{Coul}}(N) + v_{\text{xi}}(-1)$ , respectively. (The number of electrons contained in the charge density giving rise to the potential is specified in parentheses.) These potentials share the Coulomb potential  $v_{\text{Coul}}(N)$  of  $N$  electrons. In the HF case this is augmented with the orbital-dependent exchange potentials  $v_{x,i}$

$$v_{x,i}^{\text{HF}}(\mathbf{r}_1) = \int \frac{h_{x,i}(\mathbf{r}_2; \mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 = v_i^{\text{si}}(\mathbf{r}_1) + v_{xi}^{\text{rest}}(\mathbf{r}_1). \quad (4)$$

The HF exchange potential  $v_{x,i}^{\text{HF}}$  has been written as the self-interaction potential  $v_i^{\text{si}}(\mathbf{r}_1) = -\int |\phi_i(\mathbf{r}_2)|^2 d\mathbf{r}_2 / |\mathbf{r}_1 - \mathbf{r}_2|$  of the electron in the considered occupied MO, plus a rest term. The self-interaction part of the exchange hole integrates to  $-1$  electron, the rest of the hole integrates to zero electrons. From the similar orbital energies of the occupied orbitals it may already be surmised that also the xc part of the KS potential

will be due to a hole charge of  $-1$  electron. Closer examination of the KS potential shows this to be true. We may use the full exchange–correlation hole  $h_{xc}(\mathbf{r}_1, \mathbf{r}_2)$  of the exact wavefunction, which may be expressed *via* the exchange–correlation part of the (diagonal of the) two-particle density matrix  $\Gamma_{xc}$ , or with the pair correlation function  $g(\mathbf{r}_1, \mathbf{r}_2)$ ,

$$\begin{aligned} h_{xc}(\mathbf{r}_1, \mathbf{r}_2) &= \frac{\Gamma(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)} - \rho(\mathbf{r}_2) \equiv \frac{\Gamma_{xc}(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)} \\ &= \rho(\mathbf{r}_2)(g(\mathbf{r}_1, \mathbf{r}_2) - 1) \\ \forall \mathbf{r}_1 \int h_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 &= -1 \\ v_{xc}^{\text{hole}}(\mathbf{r}_1) &= \int \frac{h_{xc}(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \end{aligned} \quad (5)$$

so that the full exchange–correlation energy becomes

$$\begin{aligned} W_{xc} &= \frac{1}{2} \int (\Gamma(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)) \frac{1}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \\ &\equiv \frac{1}{2} \int \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)(g(\mathbf{r}_1, \mathbf{r}_2) - 1) \frac{1}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \\ &\equiv \frac{1}{2} \int \rho(\mathbf{r}_1) v_{xc}^{\text{hole}}(\mathbf{r}_1) d\mathbf{r}_1 \end{aligned} \quad (6)$$

The exchange–correlation energy  $E_{xc}$  of DFT also contains the kinetic correlation energy  $T - T_s$ , which can be written with the kinetic energy densities  $\nu_{\text{kin}}(\mathbf{r})$  and  $\nu_{s,\text{kin}}(\mathbf{r})$  (subscript  $s$  refers to the KS system), or  $\nu_{c,\text{kin}}(\mathbf{r}) = \nu_{\text{kin}}(\mathbf{r}) - \nu_{s,\text{kin}}(\mathbf{r})$ ,<sup>35,36</sup>

$$\begin{aligned} E_{xc} &= W_{xc} + T - T_s \\ &= \frac{1}{2} \int \rho(\mathbf{r}) \nu_{xc}^{\text{hole}}(\mathbf{r}) d\mathbf{r} + \int \rho(\mathbf{r}) (\nu_{\text{kin}}(\mathbf{r}) - \nu_{s,\text{kin}}(\mathbf{r})) d\mathbf{r} \\ \nu_{xc}(\mathbf{r}) &= \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} = v_{xc}^{\text{hole}}(\mathbf{r}) + \nu_{c,\text{kin}}(\mathbf{r}) + v^{\text{resp}}(\mathbf{r}) \end{aligned} \quad (7)$$

The leading term in the KS potential is the xc hole potential.  $v^{\text{resp}}(\mathbf{r})$  contains the terms that arise from the differentiation of the kinetic energy densities and the pair correlation factor. This potential as well as the kinetic potentials have been analyzed before.<sup>24,35–38</sup> These potentials are responsible for important features of the exact KS potential, such as the step behavior in going from one atomic shell to the next (from  $v^{\text{resp}}$ <sup>38,39</sup>), the bond midpoint peak when a molecule is dissociating (from  $\nu_{\text{kin}}$ <sup>35</sup>), and the step behavior in the KS potential towards the atom with highest ionization energy when a system consisting of two different separate atoms is considered (from  $v^{\text{resp}}$ <sup>40</sup>), vestiges of which even exist at equilibrium bond length.<sup>31</sup> The occurrence of such steps had originally been deduced by Perdew<sup>41</sup> and Almbladh and von Barth.<sup>42</sup> However, in a molecule the potentials  $\nu_{c,\text{kin}}(\mathbf{r}) = \nu_{\text{kin}}(\mathbf{r}) - \nu_{s,\text{kin}}(\mathbf{r})$  and  $v^{\text{resp}}(\mathbf{r})$  yield relatively small contributions for the upper valence orbitals, and in particular they go to zero in the outer region of a molecule (in the outermost shell of an atom). In this paper we focus on the consequences of the presence of the hole potential in the KS potential. This is an attractive potential due to a  $+1$  charge (the hole integrates to  $-1$  electron). This hole

“follows” the electron: at each position  $\mathbf{r}_1$  at which the potential is considered it is localized around that position, even more so than the HF exchange hole, see *e.g.* the plots of the exchange hole and total exchange–correlation hole in the simple two-electron bond of  $\text{H}_2$  in ref. 43–45. Its influence is therefore strong. This statement does not hold in the asymptotic regions of the molecule: in those regions the hole remains behind in the molecular region, which is why the asymptotic behaviors of the hole potential and KS potential become  $-1/r$ .

We note that the shape of the KS potential endows the KS orbitals with excellent properties. Not only do the orbital energies have a direct connection with ionization potentials, also the shapes of the orbitals are very good. It is not an exaggeration to state that the determinant built from occupied KS orbitals (even though, of course, it still lacks correlation) is a “better” wavefunction than the HF determinant: its energy is only very slightly higher than the energy of the HF determinant, while individual energy terms like kinetic energy, electron–nuclear energy and electron–electron repulsion energy are much better.<sup>32,36,46</sup> This is why KS orbitals are excellently suited for qualitative (semi-quantitative) molecular orbital theoretical considerations.<sup>47,48</sup> Such praise for the KS orbitals can be extended to the virtual orbitals, see the following sections.

### 3. Orbital energies of virtual orbitals

We now turn to the issue of the meaning of the energies of the KS virtual MOs. The virtual KS orbitals are one-electron states having exactly the same (local) potential as the occupied orbitals. They represent excited electrons in the noninteracting KS reference system. The local potential represents a Coulomb field of  $N$  electrons plus an exchange–correlation hole of  $-1$  electrons. The excited electron “sees” this same field of  $N - 1$  electrons as do the ground state electrons. This is very different from the Hartree–Fock model. In the Hartree–Fock model the potential for the virtual orbitals has lost the stabilizing hole potential, the virtual orbitals see one electron more ( $N$  instead of  $N - 1$ ) than the occupied orbitals. Accordingly, the Hartree–Fock orbitals are shifted to much higher energy than the virtual KS orbitals are, and they are much more diffuse (see below). Physically one might expect the HOMO–LUMO gap in the KS case to be a good approximation to the lowest excitation energy of the system. Invoking again the “exact” KS calculations, it is observed in Table 2 that the exact KS gaps indeed are very close to the lowest excitation energies, *i.e.* the optical gap  $\Delta_{\text{opt}}$ . This is a great asset of the KS model – largely preserved in DFA’s like LDA and GGA, see below – that we feel should be cherished rather than discarded. While the KS and HF HOMO energies resemble each other, the HF LUMO energies differ greatly from the KS ones (See Table 3). The HF LUMOs of the considered molecules are all unbound in the chosen basis with positive energies in the range  $+0.8$  to  $+3.2$  eV. The KS LUMOs are all substantially bound with energies in the range  $-5.1$  to  $-6.8$  eV. This large stabilization compared to the HF LUMO energies reveals the fundamental difference of the KS spectrum and the HF spectrum. The KS orbitals are genuinely bound one-electron states.



**Table 2** Comparison of the KS, HF and BLYP HOMO–LUMO gaps (basis set: aug-cc-pVTZ) and the experimental lowest vertical optical excitation energy, eV. For N<sub>2</sub> the energy of the occupied 1 $\pi_u$  orbital is inserted in the orbital energy difference, even when it is not the HOMO, since the optical gap corresponds to the 1 $\pi_u$  → 1 $\pi_g$  excitation. For N<sub>2</sub> the experimental energies give the range of <sup>1</sup> $\Sigma$ , <sup>1</sup> $\Pi$  and <sup>1</sup> $\Delta$  states of the 1 $\pi_u$  → 1 $\pi_g$  transition. The FCN “experimental” excitation energies are from this work (CCSD calculations in the aug-cc-pVQZ basis)

	$\epsilon_L^{\text{HF}} - \epsilon_H^{\text{HF}}$		$\epsilon_L^{\text{LDA}} - \epsilon_H^{\text{LDA}}$		$\epsilon_L^{\text{BLYP}} - \epsilon_H^{\text{BLYP}}$		$\epsilon_L^{\text{KS}} - \epsilon_H^{\text{KS}}$		Expt. excitation energy		Ref.
									Singlet	Triplet	
H <sub>2</sub>	17.6	10.6	10.5	12.5	12.7	11.7	(FCI)				
H <sub>2</sub> O	14.7	6.5	6.2	7.5	7.65	7.5	52				
HF	18.5	8.9	8.5	10.5	10.3	9.9	53				
N <sub>2</sub>	19.9	9.7	9.6	9.9	9.3–10.3	7.8–8.9	54				
CO	17.0	6.9	7.1	7.5	8.5	6.3	51				
HCN	15.4	7.9	7.8	8.0	8.8	6.2	55				
FCN	14.8	7.3	7.0	7.6	8.4	7.8	This work				
HCl	13.8	7.0	6.8	7.4	7.8	7.4	56				

**Table 3** KS and HF HOMO and LUMO orbital energies, eV. Basis set: aug-cc-pVTZ

	HOMO				LUMO			
	HF	LDA	BLYP	KS	HF	LDA	BLYP	KS
H <sub>2</sub>	−16.18	−10.26	−10.39	−16.44	+1.42	+0.31	+0.12	−3.93
H <sub>2</sub> O	−13.88	−7.40	−7.21	−12.62	+0.80	−0.92	−1.06	−5.11
HF	−17.69	−9.82	−9.64	−16.19	+0.81	−0.93	−1.13	−5.71
N <sub>2</sub>	−16.71	−11.89	−11.49	−16.68	+3.19	−2.21	−1.91	−6.77
CO	−15.10	−9.11	−9.00	−14.01	+1.88	−2.24	−1.94	−6.56
HCN	−13.50	−9.23	−8.87	−13.61	+1.93	−1.33	−1.07	−5.53
FCN	−13.65	−8.97	−8.62	−13.67	+1.16	−1.66	−1.59	−6.01
HCl	−12.98	−8.15	−7.91	−12.77	+0.79	−1.11	−1.15	−5.36

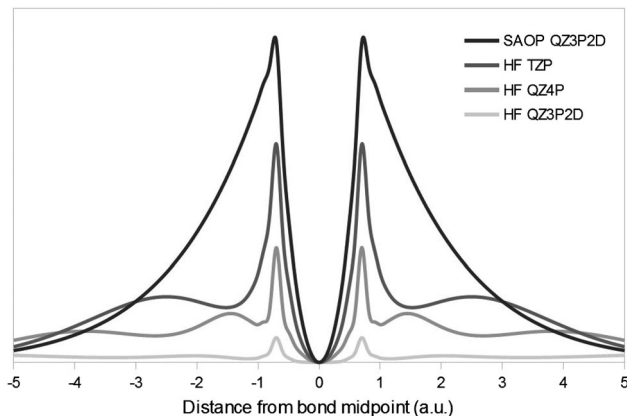
Their shapes describe the excited state very well, as exemplified by the fact that TDDFT calculations typically give a very simple interpretation of excitations as consisting of one or a few single-orbital transitions. An example is given in ref. 49 for the excited states of N<sub>2</sub>, where a whole series of excitations can be described as almost 100% single orbital transitions in the KS MO basis. The reason is that the KS virtual orbitals (and similarly the SAOP orbitals used in ref. 49) are genuinely bound orbitals that do describe excited electrons. (The statistical average of orbital dependent potentials (SAOP)<sup>50,51</sup> is a good approximation to the exact KS potential, with the eigenvalue spectrum close to the true KS one.<sup>22,49</sup>) Even the LDA or GGA virtual orbitals are often bound and have reasonable shapes, except for the higher lying ones, which get distorted. The LDA and GGA orbitals, although considerably upshifted with respect to the KS orbitals, still have energies below zero (except for H<sub>2</sub>), *i.e.* are bound one-electron states, with still reasonable shapes. Nevertheless, the upshift and the too fast decay to zero of the LDA/GGA potential distorts the orbital shapes, notably of the higher lying ones that approach zero energy from below, including the Rydberg-like orbitals. This manifests itself in particular in poorer oscillator strengths of the corresponding transitions, see discussion in ref. 49. We note that the good shape of the KS virtual orbitals is not accidental: the orbital describing the excited electron should see a hole charge (integrating to +1) representing the “hole” it left behind. The KS

virtual orbital sees, in fact, the same exchange–correlation hole as the occupied orbitals, which is determined by the exchange–correlation phenomenon. At a position *r* both occupied and virtual orbitals feel the KS hole, which is localized around *r*. In small and medium sized molecules the deviation of this exchange–correlation hole from the physical hole due to the excitation is much less important than the fact that both have a charge +1 and exert a strongly stabilizing effect. This is depicted in the left panel of Fig. 3: in a compact molecule or for a localized excitation the xc hole is a reasonable representation of the actual “depletion hole” of the excitation and the strong stabilization of the virtual KS orbitals by the “pull” of the xc hole is physically similar to the “pull” by the actual depletion hole. This will no longer hold if there is a physical dislocation between the KS exchange–correlation hole and the hole of the excited electron–hole pair, see Sections 6 and 7.

In contrast, the HF virtual orbitals are in many cases not bound states. They are already much too diffuse to begin with, since they represent an added electron. An electron in a virtual HF MO  $\phi_a$  interacts with *N* electrons through the resultant potential  $v_a^{\text{HF}}(N) = v_{\text{Coul}}(N) + v_{\text{xa}}^{\text{HF}}(0)$  with the orbital-dependent HF exchange potential  $v_{\text{xa}}^{\text{HF}}(0)$  representing zero charge in this case. According to Koopmans’ theorem,<sup>34</sup>  $\epsilon_L^{\text{HF}}$  is the energy of electron addition, *i.e.* the electron affinity  $-A$ , in the approximation of frozen orbitals. However, closed shell neutral molecules often do not have a (positive) electron affinity, or a very small one: they do not at all, or just barely, bind an additional electron. One has to study somewhat special cases, in particular systems with unsaturated bonds (radicals) to find EAs higher than 2 eV, see *e.g.* Table 10 in ref. 57. At the same time, the error of the frozen orbital approximation and the neglect of correlation tend to make the HF orbital energy considerably higher (less negative) than  $-A$ . Let us define the *positive* relaxation (Koopmans’) errors  $\Delta_{\text{relax}}(\text{M}^+)$  and  $\Delta_{\text{relax}}(\text{M}^-)$  as well as the *positive* correlation errors  $\Delta_{\text{corr}}(\text{M}^+)$  and  $\Delta_{\text{corr}}(\text{M}^-)$  for both ionization and electron attachment,

$$\begin{aligned}
 E_{\text{corr}}(\text{M}) &= E_{\text{exact}}(\text{M}) - E_{\text{SCF}}(\text{M}) \\
 E_{\text{corr}}(\text{M}^+) &= E_{\text{exact}}(\text{M}^+) - E_{\text{SCF}}(\text{M}^+) \\
 E_{\text{corr}}(\text{M}^-) &= E_{\text{exact}}(\text{M}^-) - E_{\text{SCF}}(\text{M}^-) \\
 \Delta_{\text{corr}}(\text{M}^+) &= E_{\text{corr}}(\text{M}^+) - E_{\text{corr}}(\text{M}) \\
 \Delta_{\text{corr}}(\text{M}^-) &= E_{\text{corr}}(\text{M}) - E_{\text{corr}}(\text{M}^-) \\
 \Delta_{\text{relax}}(\text{M}^-) &= E_{\text{Koopmans}}(\text{M}^-) - E_{\text{SCF}}(\text{M}^-) \\
 \Delta_{\text{relax}}(\text{M}^+) &= E_{\text{Koopmans}}(\text{M}^+) - E_{\text{SCF}}(\text{M}^+) \\
 \epsilon_{\text{H}} &= -I - \Delta_{\text{relax}}(\text{M}^+) + \Delta_{\text{corr}}(\text{M}^+) \\
 \epsilon_{\text{L}} &= -A + \Delta_{\text{relax}}(\text{M}^-) + \Delta_{\text{corr}}(\text{M}^-).
 \end{aligned}
 \tag{8}$$

It is clear that the relaxation and correlation errors counteract in the case of the occupied orbital energy, which is in general not so far from the experimental ionization potential, typical deviations being *ca.*  $-1$  eV. (The orbital energy is more negative than  $-I$  since the relaxation is larger than the correlation



**Fig. 2** Comparison of the shape of the KS LUMO orbital density of  $H_2$  at  $R_e$  (in SAOP approximation to the KS potential) to the HF LUMO densities in a series of STO basis sets. The HF LUMO shape is not well defined, the larger the basis set the more diffuse the orbital and the lower the (positive) orbital energy, which approaches zero for infinitely extended orbital. In any finite basis set localized on the molecule the orbital energy and the shape are not realistic but entirely determined by the basis set.

energy difference between  $M^+$  and  $M$ .) However, for the Koopmans' estimate of the electron affinity the relaxation and correlation errors add up, both making the HF orbital energy higher (less negative or even positive). Because the affinity  $-A$  is so small, and the relaxation and correlation errors are significant, the HF orbital energy is often positive even when  $-A$  is negative but small (small positive electron affinity), a very common situation. Note, for instance, that in ref. 12 (Fig. 2) the HF LUMO orbital energies of the 113 investigated molecules (with the sizable 6-311++G(3df,3pd) basis set) are almost all positive. We should realize that the HF operator for an unoccupied orbital represents a potential that has attractive positive charges at the nuclei but an equally large compensating repulsive negative charge distribution of the electrons. There is no  $-1/r$  long range behavior observed. It depends on the detailed shape of the potential in the molecular region (how deficient the screening of the nuclear charges by the electron density is) whether bound states can be supported at all under such a potential. It should come as no surprise that often they can not.

If the HF operator for the virtual orbitals does not support a negative LUMO orbital energy, either because the anion is genuinely unbound, or unbound in the Koopmans' approximation, the calculation of the virtual orbital spectrum is converted into an electron scattering problem: there are scattering states for an additional electron at every energy above zero, being infinitely extended (plane wave like) at large distances from the molecule, with only a few orthogonality wiggles in the molecular neighborhood. Only at specific positive energies (actually small energy intervals) resonances will be found, with scattering states that have considerable amplitude in the molecular region. These shape resonances can be interpreted as giving information about the orbital in which an electron can be captured to form a temporary anion. Such an anion is unstable and will decay to the molecule in its ground state

(or an electronically and/or vibrationally excited state) and a free electron. When one does a calculation with a standard basis set just a number of positive orbital energies are obtained, representing a few discrete states out of the continuum at positive energy. The orbital energies are an accidental product of the basis set. The study of the resonances is an interesting topic in itself, we refer to the extensive review on alkenes and alkynes by Jordan and Burrow,<sup>58</sup> and to computational work by Jordan and coworkers<sup>59,60</sup> and Cheng and Chen<sup>61</sup> on the determination of these resonances. If one uses the typical quantum chemistry method of finite basis sets (instead of scattering calculations with *e.g.* orthogonalized plane wave methods) mostly the so-called SKT (stabilization Koopmans theorem) method of Taylor and Hazi<sup>62,63</sup> is used, and the related DOS (density of states) method of Mandelshtam, Ravuri and Taylor.<sup>64</sup> Essentially, these methods consist of a systematic variation of the given basis by scaling the exponents so as to make them increasingly more diffuse. All virtual orbital energies will then continuously go down, the lowest one approaching zero, since that is the true LUMO energy in this case. On their way down, they may cross a resonance energy, and then one can by inspection or by a more sophisticated technique signal this event and gain information about the resonance energies and corresponding orbital shapes. The lowest resonance energy is often tabulated as a negative electron affinity. Many molecules, in particular small ones, but also large molecules, have negative electron affinities, *i.e.* they do not have bound anion states with infinite lifetime, see *e.g.* compilations in ref. 65–67 (ref. 57 concentrates on positive electron affinities). The basis set used in Table 3 was the standard aug-cc-pVTZ Gaussian basis set. We illustrate the above remarks by giving in Table 4 the orbital energies for the HOMO and the LUMO of  $H_2$  in a series of Gaussian basis sets and a series of Slater type orbitals. The Gaussian sets are the standard Dunning series,<sup>68</sup> the STOs are from the ADF basis set library.<sup>69,70</sup> Note that for H the polarization functions (PD) are p and d functions, while the even-tempered ETQZ3P-2D set has 6s, 4p and 3d sets. For each  $l$  two of the sets are diffuse. It is clear that the occupied  $1\sigma_g$  orbital has a very stable HF orbital energy, already converged to a few hundredths eV at the medium quality cc-pVTZ or DZP basis sets. The virtual orbital is however very sensitive to the basis set. It drops from +18.116 eV in a single zeta STO basis set to *ca.* 5.5 eV

**Table 4** Basis set dependence of the HF HOMO and LUMO orbital energies of  $H_2$  at  $R_e$ , eV

	cc-pVDZ	cc-pVQZ	aug-cc-pV5Z	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z
Gaussian basis functions							
$1\sigma_g$	-16.113	-16.181	-16.181	-16.124	-16.175	-16.181	-16.181
$1\sigma_u$	5.368	3.912	3.144	1.673	1.424	1.279	1.139
Gap	21.482	20.662	19.325	17.797	17.598	17.460	17.320
	SZ	DZ	DZP	TZP	TZ2P	QZ4P	ETQZ3P-2D
Slater type orbitals							
$1\sigma_g$	-15.884	-16.255	-16.200	-16.207	-16.204	-16.182	-16.183
$1\sigma_u$	18.116	5.517	5.108	3.387	3.452	2.667	1.176
Gap	34.000	21.772	21.308	19.594	19.656	18.849	17

in DZ basis sets (both STO and Gaussian) and then continues down to zero, although the given basis sets (even the large Gaussian aug-cc-pV5Z and the large STO ETQZ3P-2D) are not diffuse enough to get closer than *ca.* 1 eV to zero. Note that adding diffuse basis functions in, for instance, the change from cc-pVDZ to aug-cc-pVDZ leads to a drop of *ca.* 3 eV in the LUMO orbital energy, underlining its unrealistic character. Fig. 2 presents the KS  $1\sigma_u$  orbital of the  $H_2$  molecule compared to the HF LUMO in a series of STO basis sets. The unoccupied HF orbitals rapidly become more diffuse when the basis set flexibility is increased. They are here confined to the molecular region by the use of standard atom-centered basis sets, but even so the shapes in the larger basis sets become pathetically diffuse (note that the plotted orbital densities integrate (over all space) to 1 in all cases; in the larger basis sets almost the complete density is outside the plotted window of 10 bohr). In the more diffuse basis sets the HF LUMO starts to approximate the orthogonalized plane wave type of wavefunction (wiggles at the atomic positions to generate the orthogonality to the occupied orbital) expected for a free electron in the presence of the  $H_2$  molecule. It is clear that the HF unoccupied orbital is not well defined, the HF virtual orbitals have very little relation to the excitation phenomenon. This does not mean that excited state calculations cannot be done with such a basis set: a (MR-)CI can give very good results, because the primitive basis set may very well be able to describe the bound excited state. Only its interpretation using the accidental HF virtual MOs will be problematic: the larger the primitive basis, the more accurate the calculation will be, and the more questionable the interpretation of the excited state in terms of the HF virtual orbitals.

#### 4. Density functional approximations: LDA and GGA

What about the orbital energies of common DF approximations like LDA and GGA? Table 3 compares the HOMO and LUMO energies calculated in local density (LDA) and generalized gradient (GGA-BLYP) approximations with the exact KS ones. It has been observed in both atoms<sup>16</sup> and molecules<sup>49</sup> that the standard LDA/GGA xc potentials exhibit in the atomic or molecular bulk region a fairly uniform shift upwards by several eV compared to the exact KS potential or to SAOP.<sup>51</sup> This feature of LDA/GGA is reflected in the corresponding upward shift of  $\epsilon_H^{LDA/BLYP}$ . Ref. 49 gives these upshifts for a set of 21 common molecules, for the LDA, BP86 and BLYP functionals compared to the SAOP potentials. The upshifts for each molecule are very similar for these three functionals (a few tenths of an eV different at most), so the averages over the 21 molecules are also very similar (4.5, 4.5 and 4.7 eV respectively). The variation over the molecules is significant (minimum upshift 3.2 eV, maximum (for HF molecule) 6.2 eV). The maximum upshift with respect to the exact KS potential in Table 3 is again for the HF molecule: 6.6 eV. The differences between occupied orbital energies are not much affected by the approximate

functionals, the one-electron levels of the occupied orbitals shift up almost uniformly.<sup>25</sup> Table 3 also presents the LDA and BLYP LUMO energies. The LDA/BLYP LUMOs shift up by approximately the same amount (compared to exact KS) as the occupied levels do. The LUMOs are all weakly bound with energies around  $-1$  to  $-2$  eV. The LDA and BLYP LUMO levels are actually pushed up much closer to the supposed values of the electron affinity  $-A$  than the true KS LUMOs are. This should not lead to confusion of the LUMO level in DFT with the electron affinity  $-A$ , and to the use of the KS gap to evaluate the fundamental gap  $I - A$ . The latter suggestion fails, since the LDA/GGA shift also pushes the HOMO level upwards by approximately the same amount, so that the HOMO–LUMO gap changes only little compared to the true KS one. In particular, only for the HF molecule the difference between the LDA and KS HOMO–LUMO gaps exceeds 1 eV, while for other molecules the average value of this difference is only 0.43 eV (See Table 2). So we arrive at the conclusion, that the approximate equality  $\epsilon_L - \epsilon_H \approx \Delta_{opt}$  is a characteristic feature of both the accurate KS solution and approximations, such as LDA and standard GGAs. Remarkably, in all considered cases the LDA and BLYP HOMO–LUMO gaps are a little bit smaller than the corresponding KS gaps or the reference optical gaps  $\Delta_{opt}$  (See Table 2). This makes them, if anything, less suitable for evaluation of  $\Delta_{fund}$  than the KS ones. The established relative proximity of the LDA/GGA and KS HOMO–LUMO gaps is understandable on the basis of the rather uniform upshift of the LDA/GGA potentials over the valence region of molecules (not in the core and not in the far outer region) mentioned before. This is very fortunate: the LDA/GGA gap is also a reasonable approximation to the first excitation energy. The LDA/GGA virtual-occupied orbital energy differences  $\epsilon_a - \epsilon_i$  can be used in TDDFT calculations as good approximations to the exact KS orbital energy differences on the diagonal of the leading  $E^2$  matrix of the matrix diagonalization problem of linear response TDDFT.<sup>71</sup> The matrix equations for TDDFT (time-dependent Kohn–Sham) read

$$\left(E^2 + 2\sqrt{EK}\sqrt{E}\right)F = \omega^2 F \quad (9)$$

where the  $n_{occ}n_{virt} \times n_{occ}n_{virt}$  matrix  $E$  is diagonal with the virtual-occupied orbital energy differences on the diagonal:  $E_{ia,ia} = \epsilon_a - \epsilon_i$ . The “coupling term”  $\sqrt{EK}\sqrt{E}$  in this coupled-perturbed Kohn–Sham calculation contains matrix elements of the Hartree-exchange–correlation kernel  $f_{Hxc}$ . In molecules it usually makes a relatively small contribution to the excitation energy, the leading term is the orbital energy difference  $\epsilon_a - \epsilon_i$  (note that the off-diagonal matrix elements of  $\sqrt{EK}\sqrt{E}$  couple orbital transitions like  $i \rightarrow a$  and  $j \rightarrow b$  and “correct” the simple difference  $\epsilon_a - \epsilon_i$ ). This works out quite well for valence excitations in small and medium sized molecules, and for localized excitations in large systems, because the LDA/GGA orbital energy differences are close to the KS ones (which are close to the excitation energies in these cases). This is because the virtual orbitals of valence character are in the same spatial region as the occupied orbitals, and undergo the same upshift by the approximate potentials (LDA/GGA).

Because the KS (and LDA/GGA) orbital energy gap is close to the excitation energy for valence excitations, eqn (9) works very well when the xc kernel term makes a small contribution. That is the case in practice with adiabatic LDA/GGA kernels. It is maybe a happy circumstance that its contribution is small: since *e.g.* the LDA/GGA approximation of the correlation potential  $v_c$  does not seem to bear much relationship to the true KS correlation potential,<sup>72</sup> one can hardly expect its derivative (which enters the  $f_{xc}$  kernel), to be accurate. Still, the contribution of the coupling term is so small, that when one wants to improve on LDA/GGA calculations it is more important to improve the orbital energy spectrum and the shapes of the orbitals than to improve the xc kernel. This can be deduced from calculations where, in TDDFT calculations, LDA/GGA approximations to the KS potential have been compared to “exact” KS potentials, and at the same time the coupling term contributions have been quantified to determine how much is contributed by the Hartree, exchange and correlation parts of the  $f_{Hxc}$  kernel separately.<sup>73</sup> The change in the KS potential from LDA/GGA approximations to exact is most important, the Hartree part of the coupling term comes next, and the LDA exchange and correlation parts of  $f_{xc}$  matter very little, with not even clear proof that they improve things.

However, there are several cases where the excitation energy is not well reproduced in an LDA/GGA calculation. In one case (Rydberg transitions) this is due to an error of the LDA/GGA gap (compared to the exact KS gap), *i.e.* an error in the LDA/GGA potential, in the other cases (dissociating bonds, charge transfer transitions and solids) it is due to a large contribution being needed from the xc kernel term, which is not provided by the adiabatic LDA/GGA approximation of this term (*i.e.* an error in the LDA/GGA kernel):

(1) Rydberg excitations are poorly represented with LDA/GGA calculations because the orbital energy difference is wrong. The occupied orbitals are strongly upshifted by LDA/GGA, but the Rydberg orbitals are not. They are close to zero already in the exact KS potential and are only little upshifted by the LDA/GGA potentials (remaining below zero). (The LDA/GGA potentials decay to zero just as (actually more rapidly than) the exact KS potential, so in the outer region where the Rydberg orbitals have large amplitude the difference between the LDA/GGA and KS potentials is numerically not so large.) As a consequence the differences  $\varepsilon_R - \varepsilon_i$  are (much) too small and therefore the TDDFT Rydberg excitation energies are (much) too small. A basis set problem that is reminiscent of the problem we have noted with the HF virtual orbitals with positive orbital energy now occurs. When basis sets are extended, in particular with diffuse basis functions, the many Rydberg states that exist (just) below the zero of energy will become increasingly represented among the virtual orbitals of the calculation, while their shape is not very accurate due to the too fast decay to zero of the LDA/GGA potentials. But since the LUMO and other valence virtual orbitals have been shifted up, they actually will appear in between the (spurious) Rydberg orbitals. As consequence one will find in large basis set calculations increasing contamination of the excited state spectrum with many spurious Rydberg states, see *e.g.* Fig. 2 of ref. 49. This error can be remedied by using exact

KS potentials to get the orbital energies<sup>73,74</sup> or, more practical, model potentials like SAOP<sup>51</sup> that reproduce the KS orbital eigenvalue spectrum much better than LDA/GGA do. Incidentally, the generally smaller upshift of the virtual orbitals in the LDA/GGA potential starts already to be visible in the somewhat smaller HOMO–LUMO gaps with LDA/GGA than with exact KS: the LUMO shifts up a bit less than the HOMO does.

(2) A dissociating electron-pair bond exhibits wrong behavior of the excitation energies at elongated distances. The orbital energies of the bonding and antibonding orbital approach each other, *i.e.* the gap becomes zero (both with exact KS and LDA/GGA potentials). Because the contribution of the LDA/GGA xc kernel is erroneously zero in this case, LDA/GGA TDDFT fails completely in this case:<sup>75–77</sup> the excitation energy becomes zero while it should be large.

(3) Long range charge transfer transitions also suffer from the orbital energy difference (both in LDA/GGA and exact KS) being far from the actual excitation energy.

(4) Excitations in solids are typically too small because the KS gap (and also the LDA/GGA gap) is much smaller than the optical gap (often only *ca.* 50%).

The cases (3) and (4) warrant separate discussion, to be given in Sections 6 and 7 respectively. In preparation we first make a few remarks, in the next section, on the importance of the electron–hole interaction in excited states, and how this interaction is represented in various schemes.

## 5. Electron hole interaction in the excited state

An excited electron leaves a hole behind, and the electron–hole interaction has to be fully accounted for in any realistic description of the excitation energy and the excited state. The difference between the Hartree–Fock and the Kohn–Sham models demonstrates this strikingly, as expected: the HF model works with virtual orbitals (frozen orbital approximations to the excited electron wavefunctions) which lack any stabilization by a hole potential, while the KS virtual orbitals do have the stabilization from the xc hole. Therefore, as we have seen, the KS HOMO–LUMO gap is a good first approximation to the excitation energy, while the HF HOMO–LUMO gap is not. That the cause of this difference is the lack of electron–hole stabilization energy in the HF orbital energy is apparent from a frozen orbital calculation of the excitation energy. Describing the simple orbital excitation  $\psi_i \rightarrow \psi_a$  (ignoring spin effects) as the difference in energy between the ground state HF determinant  $\Phi_0 = |\psi_1\psi_2 \dots \psi_i \dots \psi_N|$  and the excited determinant  $\Phi_i^a = |\psi_1\psi_2 \dots \psi_a \dots \psi_N|$ , one obtains

$$\Delta E_{\text{excit}}(i \rightarrow a) = E(\Phi_i^a) - E(\Phi_0) = \varepsilon_a^{\text{HF}} - \varepsilon_i^{\text{HF}} - J_{ia} + K_{ia} \quad (10)$$

The orbital energy of the occupied orbital,  $\varepsilon_i$ , is reasonable in the HF model (just the Koopmans approximation to the ionization energy), but the orbital energy of the virtual orbital is much too high. It lacks the stabilization from the hole attraction. This is exactly the correction being made by the  $-J_{ia}$  term,



the Coulomb attraction between the electron density  $|\psi_a|^2$  and the hole density  $|\psi_i|^2$ . We note that the hole density  $|\psi_i|^2$  could be more delocalized than the exchange–correlation hole, in particular in a large (conjugated) system. In the KS orbital energy difference, where the xc hole is localized and presumably too strongly stabilizing, we therefore have only an approximation to this stabilization. However, in compact molecules, this approximation appears to be much less serious than the frozen orbital approximation in the HF estimate (10) (the orbital  $\psi_a^{\text{HF}}$  is (much) too diffuse for the excited electron state). A simple TDDFT estimate for the excitation energy is obtained if we assume that the  $i \rightarrow a$  excitation does not mix with other excitations (single pole approximation, SPA). In that case the diagonal element in eqn (9) becomes, with  $E_{ia,ia} = \varepsilon_a - \varepsilon_i$ ,

$$\Delta E_{\text{excit}}^{\text{SPA}}(i \rightarrow a) = \varepsilon_a^{\text{KS}} - \varepsilon_i^{\text{KS}} + \langle \psi_i | f_{\text{xc}} | \psi_a \rangle \approx \varepsilon_a^{\text{KS}} - \varepsilon_i^{\text{KS}} \quad (11)$$

The contribution of the kernel term is relatively small, although it should not be neglected: it brings the excitation energies generally closer to experiment, and is moreover responsible for the singlet–triplet splitting of the excited states. The point here is that the hole attraction is already incorporated in the KS orbital energy  $\varepsilon_a^{\text{KS}}$ , so the term  $-J_{ia}$  is not needed. It is instructive to compare this to the estimate that can be obtained from a time-dependent exact exchange (TD-EXX) calculation,<sup>78</sup>

$$\Delta E_{\text{excit}}^{\text{TD-EXX}}(i \rightarrow a) \approx \varepsilon_a^{\text{EXX}} - \varepsilon_i^{\text{EXX}} + \langle \psi_a | \hat{K}^{\text{HF}} - v_x | \psi_a \rangle + \langle \psi_i | \hat{K}^{\text{HF}} - v_x | \psi_i \rangle - J_{ia} \quad (12)$$

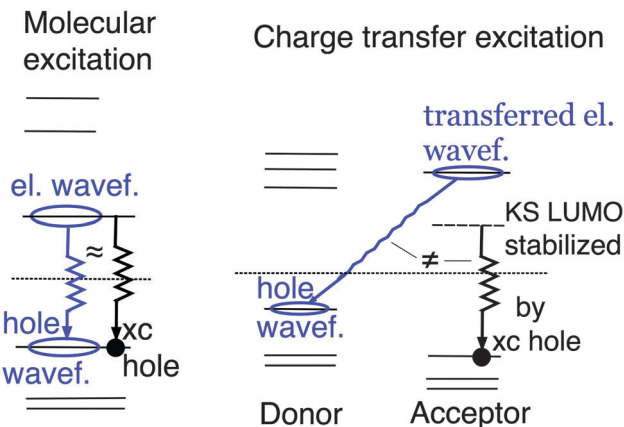
The local potential  $v_x(\mathbf{r})$  is the EXX approximation (also called the optimized potential method, OPM) to the KS potential. This is the local potential that generates the orbitals that yield (within this constraint of locality of the potential) the lowest possible energy of a determinantal wavefunction (*i.e.* the exchange energy has the same form as in Hartree–Fock). This local potential incorporates the exchange hole potential, and therefore leads to stabilized LUMO and virtual orbitals. The terms in the second line come from the TD-EXX kernel.<sup>79,80</sup> The first term in the second line of eqn (12) converts the orbital energy into a HF like value (the HF operator  $\hat{K}^{\text{HF}}$  does not have a hole potential when acting on an unoccupied orbital). The second term has obviously little correction, since  $v_x$  and  $\hat{K}^{\text{HF}}$  (for an occupied orbital) both incorporate a hole potential. As a matter of fact, this term is exactly zero for the HOMO, as shown by Krieger *et al.*<sup>81,82</sup> When the virtual orbital has been shifted up to the HF value by the first term, one needs of course the electron–hole attraction to correct this upshift, which is provided by the last term  $-J_{ia}$ . This approach may still have an advantage over HF that the unoccupied orbital is calculated in the attractive field of the exchange hole and therefore will not be inordinately diffuse, as the HF unoccupied orbital might be.

Of course, the advantages of TDDFT are not apparent when the exchange hole, or the exchange–correlation hole, is no longer a good substitute for the “depletion hole” left behind by the excited electron. In the next two sections we turn to two cases where that actually happens.

## 6. Long-range charge transfer

The issue of the interpretation of the meaning of the KS orbitals is very important for a proper understanding of the problem TDDFT has with long-range charge transfer (CT) excitations. Dreuw, Weisman and Head-Gordon found that long-range charge transfer (CT) excitations are strongly underestimated by TDDFT with LDA and GGA functionals.<sup>83</sup> The reason is immediately apparent from our previous discussion. At long range the CT energy is  $I^{\text{D}} - A^{\text{A}} - 1/R$ , where  $I^{\text{D}}$  is the ionization energy from the HOMO  $\phi_d$  of the donor molecule D,  $A^{\text{A}}$  is the electron affinity of the acceptor molecule A, where the electron goes into the LUMO  $\phi_a$ , and the  $-1/R$  term takes into account the Coulomb attraction between the positive ion  $\text{D}^+$  left behind and the negative ion  $\text{A}^-$  that has been formed. Assuming a very long distance between A and D, we ignore this term in the remainder of the discussion. The CT excitation energy should then be close to  $I^{\text{D}} - A^{\text{A}}$ , but in practice the TDDFT calculations (in the invariably used adiabatic approximation for the xc kernel) give much lower energies. This is a case where there is a large mismatch between the relevant KS orbital energy difference  $\varepsilon_a - \varepsilon_d$  and the required excitation energy: while the HOMO orbital energy  $-\varepsilon_d$  of D gives correctly the required ionization energy  $I^{\text{D}}$  (in the exact KS calculation), the KS LUMO orbital energy  $\varepsilon_a$  is far from minus the affinity of A,  $-A^{\text{A}}$ , see Fig. 1. The difference is by definition  $\Delta_{\text{L}}$  of the acceptor A. So if the coupling term makes (erroneously in this case!) little contribution, we will obtain an excitation energy that is too low by  $\Delta_{\text{L}}$ . Since TDDFT is in principle correct, this means that the coupling term in this case should make a sizable correction to the orbital energy difference. Unfortunately, the commonly used approximation of  $f_{\text{xc}}$  with LDA or GGA functionals (local, adiabatic) in this case leads to a zero contribution from the coupling term because the overlap density  $\phi_d(\mathbf{r})\phi_a(\mathbf{r})$ , which together with  $f_{\text{xc}}(\mathbf{r},\mathbf{r}')$  features in the calculation of the  $K_{da,da}$  element, goes to zero while the approximations that are commonly used for  $f_{\text{xc}}$  remain finite. The correct solution has to come from divergence in the  $f_{\text{xc}}$  kernel when  $\phi_d(\mathbf{r})\phi_a(\mathbf{r})$  goes to zero.<sup>84,85</sup>

We wish to emphasize that the error of the TDDFT CT energies is not due to the LDA or GGA approximation of the KS potential (their dependence on just the local density (gradients), or their lack of the discontinuity jump): the problem also exists with exact KS potentials (but approximate, nondiverging, kernels). If the problem would be in general a serious error in the LDA/GGA unoccupied–occupied orbital energy difference, one would have a problem in all excitation calculations (these potentials lack the discontinuity jump always). In fact, the HOMO–LUMO gap is in the CT case, as always, little affected by the choice of LDA/GGA potentials instead of the exact KS potential. Why then do we now have a mismatch of this gap and the excitation energy? Fig. 3 sketches the difference between the CT case (see the right panel) and local molecular excitations (left panel). The LUMO on the acceptor “feels” the pull of the nearby exchange–correlation hole of the KS potential of the acceptor molecule, therefore it is low-lying. That is suitable for local excitations on the acceptor molecule itself, but not for the long-range charge transfer where in reality the stabilization is



**Fig. 3** Comparison of the stabilization of the KS one-electron states (orbitals) by the local xc hole at each point, and the actual hole left behind by the excited electron, in compact molecules (the hole in same region as the excited electron, about equal stabilization) and in charge transfer excitation (much weaker stabilization by the hole at the donor remote from the electron at the acceptor).

almost absent, being due to the remote hole in the orbital on the donor that was vacated.<sup>84</sup> This is an example where there is a dislocation between the hole that is actually felt by the virtual orbital – the local exchange–correlation hole of the KS potential – and the remote physical hole of the departed electron. In such a case the stabilization of the virtual orbital in the KS potential no longer corresponds to reality, and the KS eigenvalue spectrum is not a good approximation to the excitation energy. One can discern the transition from the “normal” local excitations to charge transfer type excitations by a generalized overlap ( $S_{ia} = \int |\phi_i(\mathbf{r})|^2 |\phi_a(\mathbf{r})|^2 d\mathbf{r}$ <sup>84</sup> or  $S_{ia} = \int |\phi_i(\mathbf{r})| |\phi_a(\mathbf{r})| d\mathbf{r}$ <sup>86</sup>) going to zero, and accordingly correct the xc kernel. Such kernel correction will have to provide a divergence which can cancel the zero differential overlap of the  $\phi_a(\mathbf{r})\phi_a(\mathbf{r})$  function and bring in the necessary correction  $\Delta_L^A$  in the kernel term.<sup>84,85</sup> But the problem with the KS orbital energies in the case of charge-transfer excitations does NOT mean that the KS orbital energies are generally problematic. The KS gap is in compact molecules a good approximation to the energy of the lowest excitation.

The problem that TDDFT has with long-range CT transitions is sometimes associated with the discontinuity in the KS potential when crossing an integer number of electrons.<sup>85,87,88</sup> Some caution should be exercised here. The fact that in this particular type of excitation one needs  $-A$  of the acceptor molecule, does not mean that one necessarily needs the discontinuity jump in the potential, or that the discontinuity “causes” or “accounts for” the CT problem: that the discontinuity jump  $\Delta_{xc}$  is equal to  $\Delta_L$  does not make the latter a consequence of the first (it rather is the other way around). At present we need information on the  $(N+1)$  system ( $\Delta_L$  or  $-A$ ) to find  $\Delta_{xc}$ . Such information is implicit in Hartree–Fock calculations, which have the LUMO at approximately  $-A$  (if  $A$  is positive), and according to the results of Hirao, Tsuneda and coworkers<sup>7,12,89</sup> and Baer, Kronik and coworkers<sup>8,11,90</sup> the range-separated hybrids also yield a very much Hartree–Fock like orbital energy spectrum. Accordingly, time-dependent Hartree–Fock (TDHF) or long-range

corrected (e.g. with range separated hybrids), LC-TDDFT or RSH-TDDFT, calculations do not have a special problem with CT excitations (and neither do Ziegler’s calculations based on a constrained variational treatment of the excited state<sup>91,92</sup>). However, within the pure KS context a Koopmans’ approximation to  $\Delta_L$ , essentially the same approximation as the HF operator makes for the affinity as unoccupied orbital energy, is as easily obtained<sup>84</sup> as from a HF or generalized KS (or HFKS, see Section 8) calculation. Using  $v_s(N)$  and  $v_s(N+1)$  for the KS potentials of the  $N$  and  $N+1$  systems respectively, and writing  $\phi_L(M^-) = \phi_L^-$  and  $\phi_L(M) = \phi_L$  it is clear that

$$\Delta_L = \varepsilon_L^- - \varepsilon_L = \langle \phi_L^- | \hat{T} + v_s(N+1) | \phi_L^- \rangle - \langle \phi_L | \hat{T} + v_s(N) | \phi_L \rangle \quad (13)$$

This is an exact expression for  $\Delta_L$ . Ignoring electron relaxation effects in the anion (Koopmans’ frozen orbital approximation), i.e. with  $\phi_L(M^-) = \phi_L(M)$  and  $\rho(M^-) = \rho(M) + |\phi_L|^2$ , we can approximate this quantity as

$$\begin{aligned} \Delta_L &\approx \langle \phi_L | v_{\text{Coul}}(|\phi_L|^2) + v_{xc}(\rho^M + |\phi_L|^2) - v_{xc}(\rho^M) | \phi_L \rangle \\ &= \langle \phi_L \phi_L | \phi_L \phi_L \rangle + \langle \phi_L | v_{xc}(\rho^M + |\phi_L|^2) - v_{xc}(\rho^M) | \phi_L \rangle \quad (14) \end{aligned}$$

The frozen orbital approximation may be more severe here than in the case of Hartree–Fock, since the unoccupied  $\phi_L$  is not so diffuse as would be appropriate for the negative ion. In large molecules, which are typically of interest in CT excitations, this may not be so serious. We note that the potentials  $v_{xc}(\rho(M^-))$  and  $v_{xc}(\rho(M))$  both incorporate the attraction of a  $-1$  electron hole. The largest part of the upshift  $\Delta_L$  comes from the self-repulsion Coulomb integral  $\langle \phi_L \phi_L | \phi_L \phi_L \rangle$ .

An alternative expression is obtained when we realize that the electron affinity is the eigenvalue of the one-electron equation for the Dyson orbital with energy dependent self-energy  $\Sigma_{xc}(\varepsilon)$ , evaluated at  $\varepsilon = -A$ ,

$$\begin{aligned} (\hat{T} + v_{\text{ext}} + v_{\text{Coul}}(\rho(M)) + \Sigma_{xc}(\varepsilon_L^-)) d_L &= \varepsilon_L^- d_L \\ \varepsilon_L^- &= -A \end{aligned} \quad (15)$$

So

$$\Delta_L = \varepsilon_L^- - \varepsilon_L \approx \langle d_L | \Sigma_{xc}(-A) - v_{xc}(\rho^M) | d_L \rangle \quad (16)$$

where we have applied as frozen orbital approximation, in the same spirit as before, the assumption that the Dyson orbital  $d_L$  will be close to the KS LUMO  $\phi_L$ . In fact, the Dyson orbital is very close to the singly occupied orbital  $\phi_L^-$  of the anion (the Dyson orbitals are in general very close to the orbitals (in a HF calculation or a KS calculation) from which the ionization takes place in the one-particle model, overlaps  $>0.999$ ,<sup>24</sup>). That means that it will be considerably more diffuse than the KS LUMO of  $M$  if  $M$  is small. So again this is a similar serious frozen orbital approximation as in eqn (14),

$$\Delta_L \approx \langle \phi_L | \Sigma_{xc}(-A) - v_{xc}(\rho^M) | \phi_L \rangle \quad (17)$$

This is a well-known equation; analogous forms were obtained by Perdew<sup>41</sup> and Sham and Schlüter,<sup>20</sup> cf. ref. 85. Note that in solids the frozen orbital approximation we mentioned is not an issue: the addition of a single electron to the infinite solid

will not change the orbitals. The simplest approximation to  $\Sigma_{xc}$  is just the Hartree–Fock exchange operator  $\hat{v}^{HF}$  (for the  $N$ -electron system),

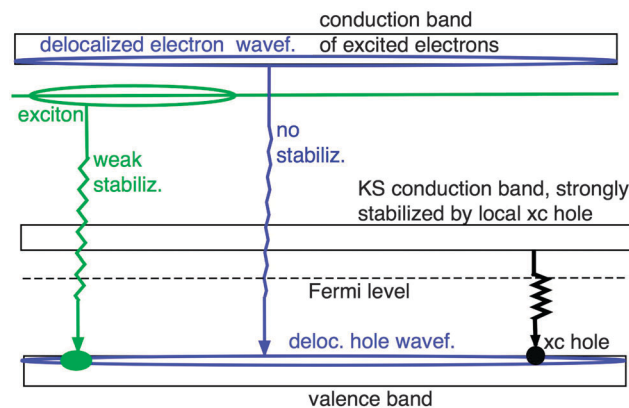
$$A_L \approx \langle \phi_L | \hat{K}^{HF} - v_{xc}(\rho^M) | \phi_L \rangle \quad (18)$$

The KS exchange–correlation potential  $v_{xc}(\rho^M)$  with its exchange hole has an attractive potential of the +1 charge of the xc hole, while the HF exchange does not represent a potential with a hole (no self-interaction correction part, its “hole” integrates to zero charge), since it acts on an unoccupied orbital. The net difference of repulsion with a charge distribution integrating to one electron is therefore also present in eqn (17) and (18), although it is not so explicitly represented as with the Coulomb integral in eqn (14).

## 7. Solids

We now consider the situation in solids. Here the statement on the “the wrong KS bandgap” originated. It denotes the fact that the KS gap – the energy difference between the highest occupied one-electron state and lowest unoccupied one – is often rather far from the fundamental gap (defined by the ionization energy and the electron affinity). The distinction between the fundamental gap and the optical gap is sometimes not clearly made, because the onset of the photoabsorption spectrum is typically close to the fundamental gap. This already indicates that there is a crucial difference between solids and molecules: in the latter the optical gap and the fundamental gap are very different. We first consider the KS gap in relation to the optical gap. Why is the KS gap much smaller in this case? The reason is analogous to the reason in the case of the long-range charge transfer transitions. The KS gap is small because of the stabilization of the unoccupied one-electron state (orbital) by the exchange–correlation hole whose potential is an important part of  $v_{xc}$ . The actual electron–hole interaction in an excited state is in a solid not well represented by this KS exchange–correlation hole. In case of a completely delocalized excitation this is clear: the actual hole is delocalized, while at each position where the KS potential is evaluated the potential of the xc hole localized around that position enters the KS potential. Therefore the KS unoccupied one-electron state is stabilized much more than the actual one-electron state containing the excited electron. In fact, since the stabilization by the completely delocalized electron hole is negligible, the distinction between an excited and an added electron gets blurred. The excitation energy will be very close to  $I - A$ . Fig. 4 shows the picture for solids, in analogy to the picture of Fig. 3 for molecules. The states of the KS conduction band experience the full “pull” of the xc hole localized around each point  $r$  where the potential is evaluated. The actual stabilization of the delocalized electron state by the delocalized hole wavefunction is on the other hand negligible.

Of course, often the lowest excited states will be excitons, which are far from being completely spread out. Typically, however, the electron–hole pair is very weakly bound. Bohr radii of Wannier–Mott excitons in semiconductors are typically a few to many nm (4.3 nm in Si). In that case the stabilization of the unoccupied KS state by the attractive potential of the local xc hole (at each position) included in the KS potential, is again not a good model for the



**Fig. 4** Comparison of the stabilization of the KS one-electron states (the conduction band) by the local xc hole at each point, and the actual hole left behind by the excited electron, in a completely delocalized excitation (no stabilization by the completely delocalized hole) and in a Wannier–Mott exciton (weak stabilization of the “large” exciton wavefunction by the hole).

stabilization of the excited electron state by the actual hole, which is rather remote on average from the excited electron. Also, there is strong dielectric screening of the actual hole–electron interaction (see sketch of Fig. 4). It is the mismatch between the full, local, stabilization by the xc hole for the KS unoccupied state on the one hand, and the weak stabilization by the actual, screened, hole that explains the discrepancy between the KS gap and the actual excitation energy. This effect of the relatively weak interaction of holes and electrons in the actual excited state is very similar to the physical dislocation of electrons and holes in the long-range charge transfer excitation we discussed for molecules. The situation may be different with the more strongly bound electron–hole pairs of Frenkel excitons. In the extreme case when a Frenkel exciton would be e.g. a local molecular excitation in a molecular solid, with very weakly interacting molecules, the situation is pretty similar to the “normal” molecular situation we have been discussing. However, a Frenkel exciton in an alkali-halide crystal is more similar to the charge-transfer case, and apart even from the solid state effects of exciton hopping and stronger screening effects, we may as little expect the KS gap to be a good measure of the excitation energy in this case as in the molecular charge transfer case.

We note that it is important to be aware that the real exchange–correlation hole is indeed localized. In molecules this is known, in particular in the case of stretched bonds the full exchange–correlation hole tends to localize at one atomic site<sup>43–45</sup> (this is in contrast to the exchange hole, which typically delocalizes over two atoms forming the (breaking) bond). There are not many accurate calculations of holes for large systems, but it has recently been established that even for conjugated molecules, or aromatic systems like benzene, where possibly some delocalization might be expected, the hole remains firmly localized over approximately one atomic site, with very little spreading out over remote sites (a little bit over the *para* C atom in benzene).<sup>93</sup> Also in solids the hole is approximately of atomic dimensions, as was shown by Louie and coworkers in calculations of the pair–correlation function in Si crystal.<sup>94</sup> The stabilization of the unoccupied KS one-electron states, which experience the attraction from this local hole,

is therefore present in solids too. Actually, the situation is not different in molecules and solids. What is different in solids is of course the nature of the excited states, which are typically much more delocalized than in molecules. The “band gap problem” is a problem of wrong expectation, or wrong interpretation of the KS gap. The KS potential is not “at fault” here. And neither are the LDA/GGA potentials. It has been speculated a long time ago that the approximations in the KS potential applied in the usual LDA/GGA calculations might be the source of the discrepancy between the KS gap and the (fundamental or optical) gap in solids. That is not the case. Very accurate calculations of the KS gap<sup>95,96</sup> reveal that the LDA/GGA calculations provide a good approximation to the KS gap, as they proved to do for molecules.

Some uncertainty about the state of affairs in solids has arisen from the consideration that adding one electron to a crystal should not make any difference to the density, and therefore to the potentials and the orbital energies. In particular the shape and energy of the orbital containing the added electron – formerly the lowest unoccupied orbital – has been supposed to be unchanged, and the orbital energy to represent the electron affinity. However, it should be recognized that when we deal with ionization and electron attachment phenomena, we need to take into account the outside world: even for a crystal of macroscopic dimensions, for which the (Kohn–Sham) Bloch states are a very good representation of the one-electron states in the bulk of the crystal, there is the outside world where the electron that is ionized has to go to. This is crucial: it is the asymptotic behavior of the potential for  $|r| \rightarrow \infty$  that sets the gauge for the potential. We use the common gauge  $v_s(\infty) = 0$  in all cases, to make the potentials comparable. The ionization energy is the energy required to bring the electron with zero kinetic energy to the outside world. The decay of the electron density will, in the KS model with a local potential, asymptotically be determined by the slowest decaying one-electron state, the top of the valence band. Therefore its one-electron energy has to be  $\varepsilon_H = -I$ . When we add a single electron to the crystal, which goes into the bottom of the conduction band, the density inside the crystal will change imperceptibly (as a percentage of the total density), but there will be a radius  $R$  far outside the crystal beyond which the density of the slowest decaying state will prevail (by enlarging  $R$  the percentage of the density coming from the added electron can be made arbitrarily large at points  $|r| > R$ ). The KS model requires the KS density to be equal to the exact density. The exact density decays according to the ionization potential of the negative system (crystal plus an added electron), which is the electron affinity of the neutral system. So one must have that  $\varepsilon_L^- = -A$  ( $\varepsilon_L^-$  stands for the one-electron energy of the state at the bottom of the conduction band which is occupied by the added electron). This can only be achieved by a uniform upshift of the KS potential inside the crystal by the constant  $\Delta = \varepsilon_L^- - \varepsilon_L$ , as has been recognized long ago.<sup>14,19,20,97</sup> The upshift will be a constant inside the crystal, since the density in each unit cell does not change, and the local KS potential that generates the density is unique. The other one-electron states, which build the density, should remain the same, and the potential should not change shape. However, the constant

upshift will not persist in asymptotic regions: outside the crystal, when the density of the added electron takes over from the bulk density, the upshift  $\Delta$  will go to zero. [We always fix  $v_s(\infty)$  at 0, to give the orbital energies an unambiguous meaning.] The argument here is very similar to the one used for the necessary upshift of the KS potential when one constructs an ensemble of an  $N$  and an  $(N + 1)$  electron system:<sup>14,19</sup> the upshift has to be a constant over the molecular or crystal region when the fraction of  $(N + 1)$  system goes to zero. And again the upshift becomes an  $r$  dependent function  $\Delta(r)$  far outside the system, which goes to zero asymptotically in order to provide the right asymptotic decay of the small fraction of  $(N + 1)$  density. But note that in the present case we are not dealing with an ensemble of  $N$  and  $(N + 1)$  electron systems, we are dealing with the integer  $(N + 1)$  electron system.

It may seem remarkable at first sight that the KS potential performs this uniform upshift over the complete crystal upon electron addition. It is not immediately obvious that such behavior follows from the expression (7) for the KS potential. The components of the potential in this expression are defined in terms of wavefunction derived quantities (notably the conditional amplitude<sup>35</sup>). The uniform upshift, however, proves to be completely consistent with expression (7) for  $v_s$ . The change in the KS potential upon electron attachment has a different origin in (small) molecules and in a crystal, although of course it puts the  $\varepsilon_L$  in both cases at  $-A$ . Addition of an electron to a molecule means that the Coulomb potential will get an additional repulsive term  $v_{\text{Coul}}[|\psi_L|^2](r_1) = +\int |\psi_L(r_2)|^2/r_{12} dr_2$ , which counteracts the hole potential  $v_{\text{xc}}^{\text{hole}}$ . If the molecule is small, the dimension of the hole charge and of  $|\psi_L|^2$  will not be very different, so the upshift of the LUMO orbital can be explained by the “annihilation” of the effect of the hole by the additional electronic charge. In a molecule the upshift of the KS potential will not be a constant over the molecular region. However, in a crystal the (almost) infinite extent of the added electronic charge means that the Coulomb potential effect is negligible. The xc hole remains fully operative. Indeed, in this case the upshift of the KS potential (by a constant in this case) can be entirely attributed not to the Coulomb potential part of  $v_s$  but to the response potential part  $v^{\text{resp}}$  of the KS potential, see eqn (7). This is reminiscent of the step behavior that the response potential exhibits when going through the shells of an atom.<sup>31,38,40,98</sup> We recall<sup>24,31,35,38,40</sup> that the response potential is defined as

$$\begin{aligned}
 v^{\text{resp}} &= v^{N-1} - v_s^{N-1} \\
 v^{N-1} &= \int \Phi^*(2 \dots N|1) \hat{H}^{N-1} \Phi(2 \dots N|1) d2 \dots dN - E_0^{N-1} \\
 v_s^{N-1} &= \int \Phi_s^*(2 \dots N|1) \hat{H}_s^{N-1} \Phi_s(2 \dots N|1) d2 \dots dN - E_{s,0}^{N-1} \\
 \Phi(2 \dots N|1) &= \frac{\Psi_0^N}{\sqrt{\rho(1)/N}}; \quad \Phi_s(2 \dots N|1) = \frac{\Psi_{s,0}^N}{\sqrt{\rho(1)/N}} \quad (19)
 \end{aligned}$$

The square of the conditional amplitude  $\Phi(2 \dots N|1)$  describes the probability to find electrons at positions  $2 \dots N$  when one electron is known to be at position 1. It incorporates all the



effects of electron correlation on the pair density.  $\Phi$  is a wavefunction for an  $(N - 1)$ -electron system, the one-electron density of which is just the conditional density to find an electron (in the  $N$ -electron system) at position 2 when one electron is known to be at 1. The conditional density is the full density  $\rho(2)$  plus the exchange–correlation hole:

$$\rho^{\text{cond}}(2|1) = (N - 1) \int \Phi^*(2, 3 \dots N|1) \Phi(2, 3 \dots N|1) d3 d4 \dots dN \\ = \rho(2) + \rho_{\text{xc}}^{\text{hole}}(2|1) \quad (20)$$

It is remarkable that this part of the KS potential, which is so intimately connected with the details of the electron correlation, still exhibits a featureless constant upshift upon electron attachment. This can, however, be deduced easily from the forms for the  $v^{N-1}$  and  $v_s^{N-1}$  potentials derived earlier.<sup>22,24,38</sup> The potential  $v_s^{N-1}$  can be cast in a simple form employing the KS orbitals and orbital energies using the determinantal form of the KS wavefunction, while the potential  $v^{N-1}$  can be put in a similar form by using the expansion of the wavefunction in all ion wavefunctions (all  $(N - 1)$ -el. wavefunctions  $\{\Psi_i^{N-1}\}$ , multiplied with the corresponding Dyson orbitals  $d_i$ , *i.e.* the Dyson expansion),

$$d_i(1) = \sqrt{N} \int \Psi_i^{N-1*} \Psi_0^N d2 \dots dN, \quad \rho(1) = \sum_i |d_i(1)|^2 \\ \sqrt{N} \Psi_0^N = \sum_i d_i(1) \Psi_i^{N-1}(2 \dots N) \\ v^{N-1}(1) = \sum_i (-I + I_i) \frac{|d_i(1)|^2}{\rho(1)} \\ v_s^{N-1}(1) = \sum_i (\varepsilon_N - \varepsilon_i) \frac{|\psi_i^s(1)|^2}{\rho(1)} \quad (21)$$

The equations for  $v^{N-1}$  and  $v_s^{N-1}$  are analogous, since the Dyson orbitals of the KS noninteracting electron system with the determinantal wavefunction are just the occupied KS orbitals (there are only  $N$  KS ion states and therefore  $N$  KS Dyson orbitals). We note that in the neutral system  $M$  the highest occupied orbital energy of the KS system,  $\varepsilon_N$ , is equal to the negative of the first ionization potential,  $-I$ . These potentials can also be written for the negative ion  $M^-$ , with of course the first ionization energy equal to  $A$  (and KS  $\varepsilon_{N+1}[M^-] = -A$ ). Then evidently when it is assumed that all  $\varepsilon_i(M^-) = \varepsilon_i(M) + A$ , one obtains

$$v_s^{N-1}[M^-](1) - v_s^{N-1}[M](1) = \sum_i^{N+1} (-A - \varepsilon_i - A) \frac{|\psi_i^s(1)|^2}{\rho[M^-](1)} \\ - \sum_i^N (-I - \varepsilon_i) \frac{|\psi_i^s(1)|^2}{\rho[M](1)} \\ = (I - A - A) \sum_i^N \frac{|\psi_i^s(1)|^2}{\rho[M](1)} \\ = (I - A - A) \text{ for } \mathbf{r}_1 \in \text{crystal} \quad (22)$$

The  $\psi_i^s$  can be chosen to be the same in the  $M^-$  and  $M$  systems because of the negligible perturbation by the additional electron.

Note that we restrict the positions  $\mathbf{r}_1$  to be inside the crystal, because for asymptotic  $\mathbf{r}_1$  the potentials go to zero. The highest term in each summation ( $N + 1$  for  $M^-$  and  $N$  for  $M$ ) drops out, so that in both cases asymptotically the numerator becomes negligible compared to the denominator for  $|\mathbf{r}| \rightarrow \infty$ . But inside the crystal  $|\psi_{N+1}^s(1)|^2$  is negligible at each point compared to  $\rho[M](1)$  and

$$|\psi_{N+1}^s(1)|^2 \ll \rho[M](1) \rightarrow \rho[M^-](1) = \rho[M](1) \\ \text{and } \frac{\sum_i^N |\psi_i^s(1)|^2}{\rho(1)} \approx 1 \text{ for } \mathbf{r}_1 \in \text{crystal} \quad (23)$$

For the  $v^{N-1}$  potentials we can assume that the addition of the single electron to the crystal does not make a perceptible change to the Dyson orbitals and the ionization potentials (the higher ones; it of course adds  $A$  as the first ionization potential). Then again

$$v^{N-1}[M^-](1) - v^{N-1}[M](1) = \sum_i^{N+1} (-A + I_i) \frac{|d_i(1)|^2}{\rho(1)} \\ - \sum_i^N (-I + I_i) \frac{|d_i(1)|^2}{\rho(1)} \\ = (I - A) \sum_i^N \frac{|\psi_i^s(1)|^2}{\rho(1)} \\ = (I - A) \text{ for } \mathbf{r}_1 \in \text{crystal} \quad (24)$$

So we conclude that

$$v^{\text{resp}}[M^-](1) - v^{\text{resp}}[M](1) = v^{N-1}[M^-](1) - v^{N-1}[M](1) \\ - (v_s^{N-1}[M^-](1) - v_s^{N-1}[M](1)) = \Delta \text{ for } \mathbf{r}_1 \in \text{crystal} \quad (25)$$

The response potential provides the constant upshift that has to occur in the KS model system for the crystal upon electron attachment, as we saw from asymptotic arguments earlier. This is of course just a proof of consistency: the KS potential of eqn (7) is consistent with the constant upshift that has to occur. Unfortunately, this does not provide a means of calculating the magnitude of  $\Delta$ . The necessary information is the electron attachment energy, which has to be obtained from an actual calculation of this property. It requires the ground state wavefunctions of a neutral system and an anion,  $\Psi_0^N$  and  $\Psi_0^{N+1}$ . For the upshift of the KS potential we also need information on the KS system, *i.e.*  $\Psi_s^N$  and  $\Psi_s^{N+1}$ . This is exactly the information that goes into the response potential, see eqn (19). The situation is the same as in molecules: the quantity  $\Delta_L$  has to be obtained from a calculation of the energy of  $M^-$  and  $M$ , *i.e.*  $A$ , and from the KS system (the KS LUMO level of  $M$ ), see Fig. 1.

This conclusion does not change when we consider the usual expression  $v_{\text{xc}} = \delta E_{\text{xc}} / \delta \rho(\mathbf{r})$ . We have discussed that

$$v_{\text{xc}}[\rho(M^-)](\mathbf{r}) - v_{\text{xc}}[\rho(M)](\mathbf{r}) = \left. \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})} \right|_{\rho(M^-)} - \left. \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})} \right|_{\rho(M)} \\ = \Delta_L \text{ for } \mathbf{r} \in \text{crystal} \quad (26)$$

It should be kept in mind that the xc potentials are functionals of the complete (not just the local) density. The functional

derivatives are taken at two different “points”,  $\rho(\mathbf{M}^-)$  and  $\rho(\mathbf{M})$  that are a full electron apart. We can without problem stick to the Hohenberg–Kohn constraint that the total number of electrons is constant, *i.e.* apply the constraints  $\int \rho(\mathbf{r}) d\mathbf{r} - N = 0$  and  $\int \rho(\mathbf{r}) d\mathbf{r} - (N + 1) = 0$  in the two cases. Such a constraint leads to an undetermined constant in the derivative (the Lagrange multiplier for the constraint).<sup>99–101</sup> This is the well-known free overall constant in the potential (over *all* space, asymptotic regions included), which we fix by always requiring the potential to be zero at  $\infty$ . The information that the functional derivative is, for points  $\mathbf{r}$  inside the crystal, in the  $\rho(\mathbf{M}^-)$  case a constant  $\Delta_L$  higher than in the  $\rho(\mathbf{M})$  case, comes from the asymptotic part of the density. This signals the strong nonlocality of the derivative as a functional of  $\rho$  (the density functional  $v_{xc}[\rho](\mathbf{r})$  is very nonlocal). This constant does not extend into the asymptotic region and is not related to the electron number constraint.

Returning to the issue of excitation energy calculations and the KS orbital energy spectrum, the conclusion is that in solids, as in the case of the molecular long-range charge transfer calculations, a much more important correction than in compact molecules has to come, in TDDFT calculations, from the xc kernel term. Often the KS gap is only 50–60% of the optical gap, so the xc kernel correction is indeed crucial. One can intuitively expect that the extended nature of solids will lead to larger effects of the essentially nonlocal nature of the  $f_{xc}(\mathbf{r}, \mathbf{r}')$  kernel than in molecules. Also the screening effects will play an important role. An insightful discussion can be found in the review by Onida, Reining and Rubio,<sup>102</sup> comparing GW and TDDFT calculations. It will not be surprising to find the conclusion that better kernels will have to be found if TDDFT is meant to become a method for the calculation of absorption spectra of solids. This effort has culminated in the nanoquanta kernel for TDDFT calculations on solid state systems, see *e.g.* ref. 103 and references therein.

## 8. Hartree–Fock and Hartree–Fock–Kohn–Sham (generalized Kohn–Sham)

Clearly, HF presents a rather different type of one-electron theory with a HOMO–LUMO gap which appears to be about twice as large as the KS gap (and the  $\Delta_{\text{opt}}$  values) in many molecules (See Table 2). The HF gap in solids appears to be much larger still, but we will restrict ourselves again to molecules. The larger Hartree–Fock gap is not surprising since, by virtue of Koopmans’ theorem,<sup>34</sup> the HF HOMO–LUMO gap provides an estimate of the fundamental gap  $\Delta_{\text{fund}}$  in the frozen orbital approximation. Recently, generalized KS (GKS) or Hartree–Fock–Kohn–Sham<sup>104</sup> approaches have received considerable attention.<sup>2,5,9,11,12,89</sup> Hartree–Fock–Kohn–Sham stems from the observation<sup>104</sup> that if one describes an electron system with the one-electron Hartree–Fock equations, there is a unique correspondence between the external potential  $v_{\text{ext}}$  and the density of the HF determinant. As a corollary, one can describe the exact density with the Hartree–Fock model with a slightly modified external potential (slightly because the Hartree–Fock

density is usually not so far from the exact density). In that case obviously  $\epsilon_{\text{H}}^{\text{HFKS}} = -I$  must hold, on account of the asymptotic density decay argument. It can be expected that the eigenvalue spectrum will be very much HF like, being governed by the same properties of the nonlocal exchange operator. Since the LDA and GGA models suffer from a strongly upshifted orbital spectrum compared to exact KS, one may exploit GKS approaches to improve the occupied level spectrum. In view of the closer proximity of the occupied HF levels to IPs (actually almost always lower than the experimental  $-I$ s, while the LDA/GGA ones are always higher), a mixing with the HF operator (*e.g.* using the range separation method or some other hybrid scheme) can help to improve the “Koopmans’ property” of the occupied orbital spectrum.<sup>4–8,12</sup> However, the LUMO orbital energy will be very different from the exact KS one, and much closer to the HF one. The name Hartree–Fock–Kohn–Sham<sup>105</sup> or even generalized Hartree–Fock, seems to be more appropriate since it conveys the message that this independent particle system has a thoroughly different eigenvalue spectrum than KS, more akin to the Hartree–Fock eigenvalue spectrum. It should be realized that the HFKS or GKS models not only destroy the attractive feature of the KS eigenvalue spectrum that it approximates the excitation spectrum, but also endow the virtual orbitals with the undesirable property that they are too diffuse, and therefore less suitable to describe excited states, see Section 3. This deficiency of the HF orbitals has been known for a long time and it has led over time to many attempts to improve these orbitals, the so-called improved virtual orbital (IVO) methods.<sup>106–111</sup> These methods have been used to improve the HF virtual orbitals for excited state and correlation calculations, *e.g.* by Davidson and collaborators<sup>106,108,109</sup> and Cooper and Pounder.<sup>110</sup> The IVO methods have as common rationale that they try to “pull” orbitals from the HF virtual space into the molecular valence region by applying additional attractive operators, such as can be provided by an exchange hole. The analogy with the KS potential is evident. Going from KS to GKS models appears to be going in the opposite direction, back towards unduly diffuse virtual orbitals.

We have demonstrated how significant the distortion of HF virtual orbitals can be in the plot of Fig. 2 for the  $\text{H}_2$  LUMO. This effect will be much weaker in large systems (porphyrins, phthalocyanines, ...), where the HF virtual orbitals will be bound, but remains undesirable: the HF virtual orbitals still are too diffuse for the description of an excited state. Remarkably, as shown by Palmieri *et al.*,<sup>112</sup> even for a positive ion like  $\text{NO}^+$ , which certainly does have a bound “anion” (the neutral NO in this case) the HF virtual orbitals are sufficiently inadequate that large gains in orbital configuration convergence can be obtained in correlated calculations by IVO orbital transformations of the virtual orbital space. The inadequacy of the HF virtual orbitals also translates into a much less straightforward interpretation of excitations: excited states that are almost purely single orbital excitations in a TDDFT calculation, may consist of many orbital excitations in the Hartree–Fock case, just to correct for the diffuseness of the virtual HF orbitals.<sup>49,113</sup> It is not clear to what extent the diffuseness of the HF orbitals

persists in hybrid DFT methods or GKS schemes where HF exchange is brought in by range separation, but given the high energies of the virtual orbitals they are doubtless much more diffuse than the KS LUMO and other KS low-lying virtual orbitals. If the orbital energy of *e.g.* the LUMO is again positive, as is often the case, exactly the same problem as with positive HF LUMO orbital energies will exist.

## 9. Concluding remarks

Summarizing, we have seen that in molecules the KS gap is a very good approximation to the optical gap (the first excitation energy), but not in solids. Neither in molecules nor in solids is the KS gap a good approximation to the fundamental gap  $I - A$ . It should come as no surprise that the KS band gap is not close to the fundamental gap  $I - A$  (nor exactly equal to an excitation energy). Such quantities originate from other equations in many-electron theory. For instance, the electron attachment and ionization energies, which are the poles of the one-electron Green's function, may be obtained from one-electron equations (the one-electron Dyson equation), with, however, instead of a simple local potential the energy dependent self-energy operator  $\Sigma_{xc}(\mathbf{r}, \mathbf{r}', \epsilon)$ .<sup>41</sup> Similarly, the excitation energies follow from the polarization propagator. The KS equations and orbitals are much more simple, they are different constructs in many-electron theory, and one may not off-hand expect their eigenvalue differences to correspond to certain physical properties (such as fundamental gap or optical gap).

One may prefer to use the Hartree-Fock(-Kohn-Sham) schemes, or to mix some HF character to a DFA, in order to get more direct access to (approximations to) the fundamental gap, because the HF exchange operator, with its strong differentiation of occupied and unoccupied orbitals, is a better approximation to the self-energy for unoccupied orbitals (though still energy independent and very approximate) than the KS potential is. This then is at the cost of losing the immediate interpretation of the occupied-unoccupied orbital energy gaps as approximate excitation energies (in molecules), which is a great advantage of the KS potential, and at the cost of increased computation time (in particular in solids) due to the nonlocal potential. It is a matter of choice or convenience which model one wants to use. However, having expounded the virtues of the KS model, we wish to emphatically reject the notion that there is "something wrong" with the eigenvalue spectrum of KS. On the contrary, it has important advantages over the HF model. As for molecules, there is probably much more interest in excitation energies than in electron affinities, *i.e.* more interest in the optical gap than in the fundamental gap. There is a tendency in the literature to consider the deviation of the KS gap from the fundamental gap as a "failure" that has to be remedied. That is wrong. It is simply a property of the KS system (of the local potential including the xc hole, *i.e.* a field of  $N - 1$  electrons also for the unoccupied orbitals) that a close approximation to the optical gap is obtained. It is simply a property of the HF model (a field of  $N$  electrons for the virtual orbitals) that an approximation of the fundamental gap is obtained (although often poor, see eqn (8) last line).

Neither of these models should be called "wrong" or "deficient". In particular it is not true that the "real" KS system (or the application of the "true functional, with proper discontinuity at the integer") would exhibit an eigenvalue spectrum that yields the fundamental gap. The local KS potential for an integer electron system is unique, it is defined (up to a uniform constant), it is a property of the exact system. The properties of the KS potential (steps on shell boundaries in atoms, bond midpoint peak in molecules, steps between atoms in hetero-nuclear systems) can be derived from the wavefunction and are related to various aspects of the electron correlation.<sup>35,38,40</sup> So is the stabilization of the virtual orbitals due to the exchange-correlation hole potential. The KS eigenvalue spectrum is a given property of the model. We have noted that, if the fundamental gap (electron affinity) is needed, it is still possible to stick to the KS model and use some approximate calculation of the quantity  $\Delta_L$ . The Koopmans' approximation of eqn (14)<sup>84</sup>

$$\Delta_L \approx \langle \phi_L | \phi_L | \phi_L \phi_L \rangle + \langle \phi_L | v_{xc}(\rho^M + |\phi_L|^2) - v_{xc}(\rho^M) | \phi_L \rangle \quad (27)$$

is very simple.

We have, both in molecules and in solids, emphasized that  $\Delta_L = \varepsilon_L^- - \varepsilon_L$  is a quantity that is determined by two integer electron systems. Exactly the same quantity  $\Delta_L$  plays an important role in the treatment of an ensemble of an  $N$  and an  $(N + 1)$  electron system, which has to be used to give meaning to the concept of fractional electron number systems<sup>14,19,20,114</sup> (see in particular the clear exposition of ref. 41). The analysis by Perdew *et al.* has revealed that a discontinuity in the KS potential occurs when an infinitesimal fraction of the  $(N + 1)$  state is admitted: over the molecular or crystal region, where the density is only changed infinitesimally the potential is shifted by a constant so as to align the LUMO level at  $-A$ . This can be understood immediately from the asymptotic decay of the electron density: the highest occupied orbital in the  $N + \delta$  system (the former LUMO with now  $\delta$  electrons) needs to have an exponential decay equal to that of the  $N + 1$  electron system, and therefore has to have a highest occupied orbital energy  $\varepsilon_L(N + \delta)$  equal to the ionization energy of the  $N + 1$  system. The upshift at  $\delta \downarrow 0$  (called  $\Delta_{xc}$ ) (over the molecule or crystal, but not in the asymptotic region) is thus equal to  $\varepsilon_L(M^-) - \varepsilon_L(M) = \Delta_L$ . However, these insights do not change the properties of the  $N$ -electron systems. In particular, it is not a consequence of the treatment of noninteger electron systems of ref. 14 that the KS  $\varepsilon_L(M)$  is "wrong", and that it should be equal to  $\varepsilon_L(M^-) = -A$  (when a "correct" KS potential were used). The treatment of the fractional electron systems has revealed that the discontinuity jump  $\Delta_{xc}$  of the KS potential is equal to the known quantity  $\Delta_L$ . It is logically not correct to say that this implies that the difference  $\varepsilon_L(M^-) - \varepsilon_L(M)$  is "caused by" or is "explained by" the derivative discontinuity jump in the KS potential. We are not aware of methods to obtain  $\Delta_{xc}$  independently, *i.e.* without either implicitly or explicitly invoking the negative ion.

The shifts  $\Delta_L$  which occur upon each electron addition leave some vestiges in the response part of the KS potential, showing up in a step structure in  $v_{resp}$ .<sup>98</sup> This has recently been exploited

by Kuisma and Rantala and coworkers,<sup>115</sup> who have extended the step structure of the GLLB model potential<sup>98</sup> for occupied states to the shift for the unoccupied state. This gives very good approximations for the fundamental gap of a series of semiconductors, calculated as  $\Delta_{\text{gap}}^{\text{KS}} + \Delta_{\text{L}}$ . This method has been used for the screening of the fundamental gaps of 5400 semiconductors which could be candidates for light harvesting.<sup>116</sup> Also in the case of charge transfer transitions one could choose to stick to KS calculations, but correct the acceptor level with the upshift  $\Delta_{\text{L}}(\text{acceptor}) - 1/R$ , which it would need in this case to become a proper affinity level. Maybe more appropriately, one can correct the xc kernel of TDDFT, which then needs again knowledge about  $\Delta_{\text{L}}$ .<sup>84,85,117</sup>

In conclusion, it is not correct to say that the KS gap is “wrong”, implying that it should be the fundamental gap. One could criticize approximate schemes (density functional approximations like LDA and GGA), if they would give wrong orbital energy gaps compared to the exact KS model. We have seen, however, that even the simple LDA and GGA approximations approximate the exact KS gap reasonably well, both in molecules (this work) and in solids.<sup>95,96</sup> For molecules the KS gaps are even physically very appealing, being good approximations to the excitation energy. As for the discrepancy between the KS gap and the fundamental gap: it is not fair to reproach the KS orbital energy difference for not being what it is not.

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