Simple quantitative estimate of the derivative discontinuity and the energy gap in atoms and molecules

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From spectroscopy to transport, there is hardly any property of a quantum many-particle system that does not in some way depend on whether there is a gap in the energy spectrum, and what the size of this gap is. The fundamental gap is a ground-state property of the N-body system, defined in terms of the ground-state energy \( E(N) \) as

\[
E_g = |E(N-1) - E(N)| - |E(N) - E(N+1)|,
\]

where \( E(N-1) - E(N) \) is the energy change upon removing the \( N \)th particle from the \( N \) particle system and \( E(N) - E(N+1) \) that upon removing the \( N + 1 \)th particle from the \( N + 1 \) particle system. In a noninteracting system, this definition reduces to the familiar energy gap between single-particle levels.

For interacting systems, approximate many-body calculations of total energies and energy gaps are typically performed within the framework of density-functional theory (DFT) or, for small finite systems, Hartree-Fock (HF) and post-Hartree-Fock methods. DFT provides, in addition to the ground-state density and related quantities, also a set of single-particle eigenvalues, the so-called Kohn-Sham (KS) spectrum.

The difference between the energy of the highest occupied and lowest unoccupied of these single-particle levels is the KS gap, which in extended systems become the band structure gap. Neither the KS nor the HF single-particle gaps correspond to the experimental gap, the former typically being too small and the latter too large.

Generally, one can write \( E_g = E_g^{KS} + \Delta_{xc} \), which defines \( \Delta_{xc} \) as the difference between the exact fundamental gap and the exact KS single-particle gap. In atomic physics and quantum chemistry, the importance of a nonzero \( \Delta_{xc} \) for chemical hardness is well known. Neglect of \( \Delta_{xc} \) has also been shown to lead to large errors in the calculation of Rydberg excitations, charge-transfer processes and transport, and the ionization probability of atoms exposed to strong electromagnetic fields. In semiconductors, approximate energy gaps calculated in DFT often drastically underestimate the experimental gap. In Mott insulators, in particular, the entire gap is due to \( \Delta_{xc} \). Recently it was pointed out that a similar discontinuity problem can also appear in the spin-DFT calculation of spin gaps in materials relevant for spintronics. The question whether the neglect of \( \Delta_{xc} \) or the error in \( E_g^{KS}_{\text{approx}} \) is responsible for the underestimate of the band gap in solids is considered in a standard textbook in the field to be ‘of tremendous practical importance’, and the calculation of \( \Delta_{xc} \) is ranked in a recent monograph as ‘certainly one of the major outstanding problems in contemporary DFT’, but no general answer is known.

In the present paper we draw attention to an alternative representation of \( \Delta_{xc} \), which casts it as a difference of single-particle eigenvalues, similar to the KS gap. We point out that this relation provides a simple physical interpretation of the elusive \( xc \) discontinuity, and use it to estimate \( xc \) discontinuities of atoms and molecules. The resulting correction \( \Delta_{xc}^{\text{est}} \) substantially improves agreement with experimental fundamental gaps, reducing the percentage deviation from experiment by more than a factor of 10 in favorable cases and by about a factor of two in less favorable ones.

The standard representation of \( \Delta_{xc} \) is based on ensemble DFT for open systems, where all three quantities in \( E_g = E_g^{KS} + \Delta_{xc} \) can be related to derivative discontinuities of universal density functionals. The fundamental gap is the derivative discontinuity of the to-
The third term, the xc discontinuity \( \Delta_{xc} \), has resisted all attempts of describing it directly by common density functionals, such as LDA and GGA, which are continuous as a function of \( N \) and thus have no \( xc \) discontinuity.

However, we note that \( I \) and \( A \) can be calculated in DFT not only from ground-state energies, but also from single-particle eigenvalues, via \( I = -\epsilon_N(N) \) and \( A = -\epsilon_{N+1}(N+1) \) (the analogue of Koopmans’ theorem in DFT) \( [1, 20] \). By using these relations and the definition of \( E_g^{KS} \) one finds, upon combining Eqs. (4) and (5) \( [21] \),

\[
E_g = \epsilon_{N+1}(N) - \epsilon_N(N) + \Delta_{xc} = \epsilon_{N+1}(N+1) - \epsilon_N(N),
\]

which implies

\[
\Delta_{xc} = \epsilon_{N+1}(N+1) - \epsilon_{N+1}(N) = A_{KS} - A. \tag{7}
\]

In the last step we used the fact that the affinity of the KS system, \( A_{KS} \), is simply the negative of the energy of the lowest unoccupied orbital.

One way to estimate \( \Delta_{xc} \) is by subtracting Eq. (5) from (4). In the following, we use Eq. (7), which is equivalent in principle, but simpler in practice \( [22] \). It also provides an intuitive interpretation of the discontinuity: in an interacting system, the electrons repel, hence the energy cost of removing the outermost electron from the negative species (which is measured by the electron affinity) is reduced, \( A < A_{KS} \), and a positive \( \Delta_{xc} \) results.

If the right-hand side of Eq. (7) could be calculated exactly, this procedure would determine the exact \( xc \) discontinuity. An estimate of \( \Delta_{xc} \) is thus obtained by using in (7) the KS eigenvalues obtained in two approximate KS calculations, one for the neutral species, the other for the anion.

Such approximate calculations involve two distinct types of errors, one associated with the approximations used for the \( xc \) functional, the other with the finite size of the basis set. As a consequence, each of the two affinities in Eq. (7) is predicted wrongly by standard combinations of functionals and basis sets. Typically, the self-interaction error inherent in common LDA and GGA type functionals shifts the eigenvalues up, in some cases so much that the anions become unbound \( [23] \). On the other hand, the finiteness of the basis set artificially stabilizes the anion \( [23] \). As a consequence of this error cancellation, practical methods for calculating affinities from LDA and GGA are available \( [23, 24, 25, 26] \).

Our key argument is that derivative discontinuities are protected from functional errors and basis-set errors by a distinct additional error compensation, independent of the one just described. Namely, Eq. (7) casts \( \Delta_{xc} \) as a difference of two affinities. Even if each is predicted wrongly on its own, their difference is expected to benefit from substantial additional error cancellation. In fact,
if all KS eigenvalues are shifted up by roughly the same amount, energy differences are preserved, and even positive eigenvalues (unbound anions) can provide reasonable discontinuities for the bound neutral system.

We call this calculation of $\Delta_{xc}$ by means of Eq. (7) an estimate, and not an approximation, to stress that it exploits an error cancellation that is hard to quantify a priori. However, in recent work on models of harmonically confined systems this estimate was found to lead to significantly improved gaps. Here we explore the performance of Eq. (7) in ab initio calculations for atoms and molecules.

In Table I we compare, for 16 light atoms, the experimental gap, the KS single-particle gap, and the DFT gap, defined as the sum of the KS gap and the estimated $xc$ discontinuity. The KS calculations were performed with the GAUSSIAN 98 program, using the B88-LYP functional and the 6−311G(d,p) basis sets. Table I shows that the error of the KS gap is significant and consistently reduced by adding the estimated $xc$ discontinuity to the KS gap, dropping by more than an order of magnitude — from 7.67eV to 0.606eV — over the data set in Table I. This large drop, together with the fact that the improvement is systematic (obtained not only on average, but in every individual case), strongly suggests that Eq. (7) is a reliable and useful way of obtaining the discontinuity.

Figure 1 is a plot of the data in Table I revealing that $\Delta_{xc}$ roughly follows the atomic shell structure. Particularly small discontinuities are found for atoms with one electron outside a closed shell, such as Li and Na. The largest discontinuities are, however, not observed for closed-shell systems but for systems one electron short of a closed shell, as is seen comparing F with Ne or Cl with Ar. We interpret this by means of Eq. (7) as a consequence of the fact that $\Delta_{xc}$ is related to two affinities, which involve negative species with one additional electron, leading to a closed shell for $F^−$ and $Cl^−$.

Specifically for the Be atom, we can further compare with independent theoretical expectations, because the discontinuity of this atom has previously been estimated by Jones and Gunnarsson (JG) by comparing the experimental gap to a near-exact KS gap obtained earlier by Pedroza and Almbladh from CI densities and approximate inversion of the KS equation. Our value $\Delta_{xc}^{be} = 5.5eV$ is encouragingly close to $\Delta_{xc,JG} = 5.7eV$.

Next, we turn to molecules. In Table II we compare our estimate of $\Delta_{xc}$ to many-body values of $\Delta_{xc}$ and to experimental fundamental gaps. The many-body discontinuity is obtained by performing coupled-cluster calculations to generate a near-exact density, followed by inversion of the KS equation to obtain the corresponding near-exact KS potential, solution of the KS equation with that potential to obtain the near-exact KS gap, and subtraction of that gap from the experimental fundamental gap. The first step is impractical for larger systems, whereas the last step involves using the experimental gap, which makes the method empirical. For these reasons, the simple estimate obtained from Eq. (7) may constitute a useful alternative, provided it turns out to be sufficiently reliable.

In fact, the estimated value of $\Delta_{xc}^{est}$ depends on the chosen basis set and functional, as well as on whether the anion geometry is separately optimized (leading to adiabatic affinities and discontinuities) or held fixed at that of the neutral species (vertical affinities and discontinuities). Tests of different combinations of methodologies indicate that best (i.e., closest to experiment) gaps are obtained if the discontinuity is calculated from vertical affinities.

Table II shows that the systems fall in two classes. For one class, comprising CO, $H_2CO$, $H_2S$, HCN, $N_2$, $PH_3$, $Cl_2$, $SO_2$, and $C_2H_4$, the gap error with respect to experiment is reduced by a similar margin as for atoms, or even more, and estimated and calculated $\Delta_{xc}$ agree well. For the other class, comprising $H_2O$, $NH_3$, HF, $CH_4$ and perhaps $C_2H_2$, the percentage error of the gap drops by a factor of two, instead of by one order of magnitude, and the estimate recovers about 50% of the many-body value of $\Delta_{xc}$. An empirical indicator of which class a system belongs to is the sign of the KS affinity: if this is negative (i.e., the lowest unoccupied KS orbital has positive eigenvalue) the system belongs to class II. We note that this is not a stability criterium because it employs the (unphysical) KS affinity and because for all molecules in Table II (with exception of $Cl_2$ and $SO_2$) the anionic species is experimentally unstable. Rather, it indicates a partial loss of the error cancellation on which our use of Eq. (7) is based. Nevertheless, even in these "unfavorable" cases, the estimate still provides a systematic improvement on the KS gap, reducing the error with respect to experiment by a factor of two. For both classes, $\Delta_{xc}^{est}$ clearly
TABLE II: Comparison of calculated and experimental gaps for small molecules. First column: experimental gap. Second column: KS single-particle gap. Third column: percentage deviation of KS gap from experimental gap. Fourth column: derivative discontinuity estimated from single-particle eigenvalues, obtained from the B88-LYP functional on the 6-311G(d,p) basis set. Fifth column: DFT gap. Sixth column: percentage deviation of DFT gap from experimental gap. Seventh column: many-body estimate of the derivative discontinuity. All values in eV.

| system | $E_{g}^{\text{expt.}}$, Ref. [32] | $E_{g}^{\text{KS}}$ | % dev. | $\Delta_{\text{est}}^{\text{KS}}$, Eq. [7] | $E_{g}^{\text{DFT}} = E_{g}^{\text{KS}} + \Delta_{\text{est}}^{\text{KS}}$ | % dev. | $\Delta_{xc}$, Ref. [31] |
|--------|-------------------------------|----------------|--------|-------------------------------|-------------------------------|--------|----------------|
| CO     | 15.8                          | 7.05           | -55.4  | 9.04                          | 16.09                         | 1.83   | 8.44           |
| H$_2$CO| 12.4                          | 3.66           | -70.5  | 8.31                          | 11.97                         | -3.43  | 8.16           |
| H$_2$S | 12.6                          | 5.68           | -54.9  | 5.33                          | 11.01                         | -12.6  | 6.53           |
| HCN    | 15.9                          | 8.06           | -49.3  | 8.24                          | 16.30                         | 2.53   | 7.89           |
| N$_2$  | 17.8                          | 8.24           | -53.7  | 9.74                          | 17.98                         | 1.15   | 9.25           |
| PH$_3$ | 11.9                          | 6.51           | -45.3  | 5.25                          | 11.76                         | -1.18  | 5.99           |
| Cl$_2$ | 9.20                          | 2.38           | -74.1  | 7.24                          | 9.620                         | 4.57   | -              |
| SO$_2$ | 11.2                          | 3.25           | -71.0  | 7.94                          | 11.19                         | -0.09  | -              |
| C$_2$H$_4$| 12.3                         | 5.76           | -53.2  | 7.10                          | 12.86                         | 4.57   | 6.53           |
| C$_2$H$_2$| 14.0                         | 6.97           | -50.2  | 5.34                          | 12.32                         | -12.0  | 7.08           |
| H$_2$O | 19.0                          | 6.47           | -66.0  | 6.15                          | 12.61                         | -33.6  | 11.4           |
| NH$_3$ | 16.3                          | 6.01           | -63.1  | 5.56                          | 11.58                         | -29.0  | 10.1           |
| HF     | 22.0                          | 8.63           | -60.8  | 6.82                          | 15.45                         | -29.8  | 11.7           |
| CH$_4$ | 20.5                          | 10.3           | -49.9  | 4.88                          | 15.15                         | -26.1  | 11.4           |

provides a quantitative correction to single-particle gaps, which may be useful in improving, e.g., the DFT description of chemical hardness [4, 5] or of transport through single molecules [8, 9].

In summary, we have cast the derivative discontinuity of DFT as a difference of two affinities, Eq. [7], and used approximate KS calculations of these to obtain estimates for the discontinuity in atoms and molecules. Our results are consistent with previous results, where available, and significantly and consistently reduce the error between calculated and measured fundamental gaps.

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