Accurate ionization potentials from Kohn-Sham eigenvalues with the help of potential adjustors

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(Dated: November 3, 2016)

Abstract

An accurate yet computationally very efficient and formally well justified approach to calculate molecular ionization potentials is presented. The first as well as higher ionization potentials are obtained as the negatives of the Kohn-Sham eigenvalues of the neutral molecule after adjusting the eigenvalues by a recently [Phys. Rev. B **91**, 245120 (2015)] introduced potential adjustor for exchange-correlation potentials. Technically the method is very simple. Besides a Kohn-Sham calculation of the neutral molecule only a second Kohn-Sham calculation of the cation is required. Then the eigenvalue spectrum of the neutral molecule is shifted such that the negative of the eigenvalue of the highest occupied molecular orbital equals the energy difference of the total electronic energies of the cation minus the neutral molecule. For the first ionization potential this simply amounts to a ΔSCF calculation. The higher ionization potentials, however, then are simply obtained as the negatives of the correspondig Kohn-Sham eigenvalues. The shift of the Kohn-Sham eigenvalue spectrum is not just ad-hoc but actually leads to the physically correct energetic adjustment of the eigenvalue spectrum as it results from emsemble density-fucntional theory. As examples the ionization potentials of a number of small molecules and of a test set of medium size organic acceptor molecules are considered with the exchange-correlation potential due to Perdew, Burke and Ernzerhof (PBE) and the hybrid functional B3LYP. The potential adjusted B3LYP eigenvalues yield ionization potentials that are in very good agreement with experimental values and that are of the same accuracy as those of various GW methods, which require substantially higher computational effort. The potential adjusted PBE eigenvalues result in somewhat less accurate ionization potential, which, however, are ...

I. INTRODUCTION

II. ENERGETIC ADJUSTMENT OF POTENTIALS

For a start, we consider the Kohn-Sham (KS) formalism for a fix integer electron number N. For simplicity we consider neutral non-spin-polarized molecules with real-valued KS orbitals. The electron number N in this case has to be even. The KS equation for the KS orbitals φ_i and their eigenvalues $\varepsilon_i[\bar{v}_s]$ is given by

$$\big[(-1/2)\nabla^2 \;+\; \bar{v}_s(\mathbf{r})\big]\;\varphi_i(\mathbf{r}) \;=\; \varepsilon_i[\bar{v}_s]\,\varphi_i(\mathbf{r}) \tag{1}$$

with the effective KS potential

$$\bar{v}_s(\mathbf{r}) \;=\; -\,\frac{\delta T_s}{\delta\rho(\mathbf{r})} \tag{2}$$

given by the functional derivative of the 'noninteracting' kinetic energy T_s, i.e., the kinetic energy of the KS model system of hypothetical non-interacting electrons, with respect to the electron density.

The bar above $\bar{v}_s$ indicates that the KS potential is defined only up to an additive constant in the KS formalism with fix integer electron number. This means $\bar{v}_s$ stands not for a single potential but for a whole set of potentials, all potentials, namely, that can be obtained by adding an arbitrary constant to one member of the set $\bar{v}_s$. The fact that the KS potential is defined only up to an additive constant is a consequence of the fact that changes $\delta\rho$ of the electron density have to integrate to zero

$$\int d\mathbf{r}\;\delta\rho \;=\; 0 \tag{3}$$

in order to keep the electron number fix. If we pick one arbitrary member $\tilde{v}_s$ out of the set $\bar{v}_s$ then the change δT_s of T_s due to a change $\delta\rho$ of the electron density is given by

$$\begin{aligned}\delta T_s &= \int d\mathbf{r}\;\tilde{v}_s(\mathbf{r})\,\delta\rho(\mathbf{r})\\ &= \int d\mathbf{r}\;\left[\tilde{v}_s(\mathbf{r})\;+\;\nu\right]\,\delta\rho(\mathbf{r})\\ &= \int d\mathbf{r}\;\bar{v}_s(\mathbf{r})\,\delta\rho(\mathbf{r})\end{aligned} \tag{4}$$

with ν denoting an arbitrary constant. The three right hand sides of Eq. (4) equal each other due to Eq. (3), which, of course, can be multiplied by any constant ν. Eq. (3) demonstrates that each member of the set of potentials $\bar{v}_s$ equally well acts as functional derivative of the kinetic energy T_s with respect to the electron density, or, the other way around, the functional derivative of T_s is to be identified with the whole set of potentials $\bar{v}_s$. It is important to realize that this is a simple mathematical consequence of the fact that the electron number is fix, in the KS formalism with fix integer electron number, the undefined additive constant in the KS potential has nothing to do with a Lagrange multiplier or a chemical potential in this case.

The KS potential is given as sum

$$\bar{v}_s(\mathbf{r}) \;=\; v(\mathbf{r}) \,+\, \bar{v}_H(\mathbf{r}) \,+\, \bar{v}_{xc}(\mathbf{r}) \tag{5}$$

of the external potential v, usually the potential of the nuclei, the Hartree potential

$$\bar{v}_H(\mathbf{r}) \;=\; \frac{\delta U}{\delta \rho(\mathbf{r})}\,, \tag{6}$$

and the exchange-correlation potential

$$\bar{v}_{xc}(\mathbf{r}) \;=\; \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \tag{7}$$

with the Coulomb energy U and the exchange-correlation energy E_{xc}. The Hartree and the exchange-correlation potential are again undefined up to an additive constant in the KS formalism with fix integer electron number for the same reason as the effective KS potential. That is $\bar{v}_H$ and $\bar{v}_{xc}$ represent sets of potentials obtained by adding arbitrary constants to one member of the set.

In order to determine the absolute energetic positions of the potentials $\bar{v}_s$, $\bar{v}_H$, and $\bar{v}_{xc}$ we have to turn to the ensemble KS formalism. A straightforward definition for the Coulomb energy in the ensemble KS formalism is $U[\rho] \;=\; \int d\mathbf{r}d\mathbf{r}'\, \rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$ which can be evaluated for any electron density including those integrating to noninteger electron numbers. The Hartree potential in the ensemble KS formalism then is given by the classical electrostatic potential $v_H(\mathbf{r}) \;=\; \int d\mathbf{r}'\, \rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$ of the electron density. In the ensemble KS formalism, the Hartree potential $v_H(\mathbf{r})$ is completely defined without the freedom of adding an abitray constant. The above Hartree potential, of course, is the one usually used in practice.

Determining the exchange-correlation potential in the ensemble KS formalism is more difficult. In the ensemble KS formalism the exchange-correlation potential is known to have a derivative discontinuity at integer electron numbers. Because typically exchange-correlation potentials are required at integer electron numbers, two limits have to be considered for the exchange-correlation potential, (i) coming from the electron deficiency side corresponding to the limit

$$v_{xc}^{N-}(\mathbf{r}) = \lim_{q\to N_-} \frac{\delta E_{xc}}{\delta\rho(\mathbf{r})} \tag{8}$$

and (ii) coming from the electron surplus side corresponding to the limit

$$v_{xc}^{N+}(\mathbf{r}) = \lim_{q\to N_+} \frac{\delta E_{xc}}{\delta\rho(\mathbf{r})} \,. \tag{9}$$

Here $\lim\limits_{q\to N_-}$ shall be the limit of the noninteger number q of electrons approaching the integer number N from below while $\lim\limits_{q\to N_+}$ denotes the limit of q approaching N from above. There are three possibilities two determine the potentials v_{xc}^{N-} and v_{xc}^{N+}. All three yield the same result for the unknown exact exchange-correlation functional but have a very different outcome for approximate functionals:

(1) The potentials v_{xc}^{N-} and v_{xc}^{N+} are obtained by taking the functional derivatives (8) and (9) of the exchange-correlation energy of the ensemble KS formalism. This is the obvious route to the potentials v_{xc}^{N-} and v_{xc}^{N+} following their definitions. It requires, however, reliable approximations for the exchange-correlation functional of the ensemble KS formalism. Exchange-correlation functionals within the local density approximation (LDA) as well as the generalized gradient approximation (GGA) can be evaluated for any electron density including those integrating to noninteger electron numbers. Therefore, in practice, LDA and GGA functionals usually are considered as approximate ensemble exchange-correlation functionals. This approximation, however, is an unphysical one because the functional derivative of LDA and GGA energies with respect to the electron density does not exhibit an integer discontinuity. This means the common practice to calculate LDA or GGA exchange-correlation potentials is fundamentally flawed and therefore questionable.

(2) In case of finite nonperiodic electronic systems the potential v_{xc}^{N-} can be obtained

from any member of the set of exchange-correlation potentials $\bar{v}_{xc}$ of the KS formalism with fix integer electron number by simply adding a constant such that the potential vanishes at infinity. The justification is that the exact potential v_{xc}^{N-} vanishes far away from a finite nonperiodic electronic system. For LDA and GGA functionals this approach has the same outcome as approach (i) discussed above. However, apart from the fact that only v_{xc}^{N-} but not v_{xc}^{N+} is accessible in this way, this approach is not well-suited for LDA of GGA functionals. The reason is simple that LDA and GGA potentials decay exponentially with the electron density for large distances from the center of charge which is fundamentally wrong. The true exchange-correlation potential decays as $1/r$ with r being the distance from the center of charge. Relying on a qualitatively wrong asymptotic when adjsting the energy of a potential obviously is not advisable.

(3) Following Ref. [1], the potentials v_{xc}^{N-} and v_{xc}^{N+} can be determined by potential adjustors from any member of the set of exchange-correlation potentials $\bar{v}_{xc}$ according to

$$v_{xc}^{N-}(\mathbf{r}) = \bar{v}_{xc}(\mathbf{r}) + \Delta_{xc}^{N-}[\bar{v}_{xc}] \tag{10}$$

with the potential adjustor

$$\Delta_{xc}^{N-}[\bar{v}_{xc}] = E_0^N - E_0^{N-1} - \varepsilon_{HOMO}[v + v_H + \bar{v}_{xc}]\,. \tag{11}$$

and according to

$$v_{Hxc}^{N+}(\mathbf{r}) = \bar{v}_{xc}(\mathbf{r}) + \Delta_{xc}^{N+}[\bar{v}_{xc}] \tag{12}$$

with the potential adjustor

$$\Delta_{xc}^{N+}[\bar{v}_{xc}] = E_0^{N+1} - E_0^{N} - \varepsilon_{LUMO}[v + v_H + \bar{v}_{xc}]\,. \tag{13}$$

In Eqs. (11) and (13), E_0^N, E_0^{N-1}, and E_0^{N+1} are the electronic ground state energies of the N-, the $(N-1)-$, and the $(N+1)$-electron system. This means, in order to calculate the potential adjustor, self-consistent KS calculations of the cation and the anion have to be carried out. By $\varepsilon_{HOMO}[v + v_H + \bar{v}_{xc}]$ and $\varepsilon_{LUMO}[v + v_H + \bar{v}_{xc}]$ the eigenvalues of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the neutral molecule are denoted. Any member of the set $\bar{v}_{xc}$ of exchange-correlation potentials can be chosen and yields the same adjusted potentials v_{xc}^{N-} and v_{xc}^{N+}. The only requirement is consistency. That is, when calculating the eigenvalues $\varepsilon_N[v + v_H + \bar{v}_{xc}]$ and $\varepsilon_{N+1}[v + v_H + \bar{v}_{xc}]$ that member of the set $\bar{v}_{xc}$ has to be used which is then adjusted via Eqs. (10) and (12). In the LDA or GGA case the simplest choice for a member of the set $\bar{v}_{xc}$ is the one resulting from the usual straightforward functional derivative of the LDA or GGA energy functional. In constrast to approaches (1) and (2) this third approach to calculate v_{xc}^{N-} and v_{xc}^{N+} is well-suited for LDA or GGA functionals for several reasons. Firstly, for any finite system different potentials v_{xc}^{N-} and v_{xc}^{N+} are obtained, that is, the LDA and GGA exchange-correlation potentials exhibit a derivative discontinuity as they should they are if constructed according to approach (3). Secondly, it is known that, for molecules, energy differences $E_0^N - E_0^{N-1}$ and $E_0^{N+1} - E_0^N$, which correspond to the negatives of the first ionization potential and the first electron affinity, can be calculated with good accuracy by ΔSCF (Δ-Self-Consistent-Field) calculations using LDA or GGA functionals. A third advantage of approach (3), which is beneficial not only for LDA and GGA functionals but generally, is that v_{xc}^{N-} and v_{xc}^{N+} are obtained exclusively from quantities that are accessible within the KS formalism of fix integer electron number, despite the fact that the potentials v_{xc}^{N-} and v_{xc}^{N+} are defined in the ensemble KS formalism. Moreover, keep in mind that Eqs. (10) – (13) are exact equations. Approximations only are introduced by the approximate functionals they are applied to.

III. ENERGETIC ADJUSTMENT OF EIGENVALUE SPECTRA

If the exchange-correlation potential is adjusted then this leads to a corresponding adjustment of the KS eigenvalues. The KS equation (1) turns into

$$\begin{aligned}\left[(-1/2)\nabla^2 + v_H(\mathbf{r}) + v_H(\mathbf{r}) + \bar{v}_{xc}(\mathbf{r}) + \Delta_{xc}^{N-}[\bar{v}_{xc}]\right] \varphi_i(\mathbf{r}) &= \left[(-1/2)\nabla^2 + \bar{v}_s(\mathbf{r}) + \Delta_{xc}^{N-}[\bar{v}_{xc}]\right] \varphi_i(\mathbf{r}) \\ &= \left[\varepsilon_i[\bar{v}_s] + \Delta_{xc}^{N-}[\bar{v}_{xc}]\right] \varphi_i(\mathbf{r}) \\ &= \left[\varepsilon_i[v + v_H + \bar{v}_{xc}] + \Delta_{xc}^{N-}[\bar{v}_{xc}]\right] \varphi_i(\mathbf{r}) \\ &= \varepsilon_i^{N-} \varphi_i(\mathbf{r}) \qquad (14)\end{aligned}$$

if the exchange-correlation potential is adjusted with the potential adjustor $\Delta_{xc}^{N-}[\bar{v}_{xc}]$ of Eq. (11). The adjusted KS eigenvalues ε_i^{N-} are given by

$$\varepsilon_i^{N-} = \varepsilon_i[v + v_H + \bar{v}_{xc}] \; + \; \Delta_{xc}^{N-}[\bar{v}_{xc}] \; = \; \varepsilon_i[\bar{v}_s] \; + \; \Delta_{xc}^{N-}[\bar{v}_{xc}] \, . \tag{15}$$

The adjusted eigenvalues ε_i^{N-} are independent of the choice which member of the set of potentials $\bar{v}_{xc}$ is used in Eq. (15), i.e., Eq. (15) yields the same adjusted eigenvalues ε_i^{N-} for all members of the set $\bar{v}_{xc}$. That means the adjusted eigenvalues ε_i^{N-} are uniquely defined. The reason is that the addition of a constant to a potential of the set $\bar{v}_{xc}$ leads to a corresponding change in the opposite direction in the potential adjustor $\Delta_{xc}^{N-}[\bar{v}_{xc}]$, see Eq. (11), and therefore in summary has no effect in Eq. (15).

For the HOMO eigenvalue we obtain

$$\begin{aligned} \varepsilon_{HOMO}^{N-} &= \varepsilon_{HOMO}[v + v_H + \bar{v}_{xc}] \; + \; \Delta_{xc}^{N-}[\bar{v}_{xc}] \\ &= \varepsilon_{HOMO}[v + v_H + \bar{v}_{xc}] \; + \; E_0^N - E_0^{N-1} - \varepsilon_{HOMO}[v + v_H + \bar{v}_{xc}] \\ &= E_0^N - E_0^{N-1} \end{aligned} \tag{16}$$

with Eq. (11) for $\Delta_{xc}^{N-}[\bar{v}_{xc}]$. This means the HOMO eigenvalue equals the negative of first ionization energy given by $E_0^N - E_0^{N-1}$ as it should. In the case of LDA or GGA functionals the negative of the adjusted HOMO eigenvalue, equals the first ionization potential calculated by a ΔSCF calculation with the LDA or GGA functional. This means Eq. (16) holds true not only for the exact functional but also for LDA or GGA functionals provided the exchange-correlation potentials and subsequently the KS eigenvalues are correctly adjusted energetically. Technically the adjustment of the KS eigenvalue spectra can be simply achieved by calculating the first ionization potential via a ΔSCF calculation and by then shifting the original eigenvalue spectrum such that the negative of the HOMO eigenvlaue equals the first ionization potential. As already mentioned, the crucial point is that this is not just an ad-hoc shift but it is the formally correct adjustment of the KS eigenvalue spectrum for the case of approaching the integer electron number N from below which is the case relevant for ionization. For the first ionization potential the approach to determine ionization energies from energetically adjusted KS eigenvalue is tantamount to the well-known ΔSCF approach. However, having at hand an eigenvalue spectrum that is properly adjusted energetically, it is promising to approximate higher ionization potentials from the negatives of the energetically lower occupied KS eigenvalues. This is what is proposed in this work and what is shown to work extremly well in the following section.

If the exchange-correlation potential is adjusted with the potential adjustor $\Delta_{xc}^{N+}[\bar{v}_{xc}]$ from Eq. (13) then the KS equation (1) turns into

$$\begin{aligned}\left[(-1/2)\nabla^2 + v_H(\mathbf{r}) + v_H(\mathbf{r}) + \bar{v}_{xc}(\mathbf{r}) + \Delta_{xc}^{N+}[\bar{v}_{xc}]\right] \varphi_i(\mathbf{r}) &= \left[(-1/2)\nabla^2 + \bar{v}_s(\mathbf{r}) + \Delta_{xc}^{N+}[\bar{v}_{xc}]\right] \varphi_i(\mathbf{r}) \\ &= \left[\varepsilon_i[\bar{v}_s] + \Delta_{xc}^{N+}[\bar{v}_{xc}]\right] \varphi_i(\mathbf{r}) \\ &= \left[\varepsilon_i[v + v_H + \bar{v}_{xc}] + \Delta_{xc}^{N+}[\bar{v}_{xc}]\right] \varphi_i(\mathbf{r}) \\ &= \varepsilon_i^{N+} \varphi_i(\mathbf{r}) \end{aligned} \tag{17}$$

The adjusted KS eigenvalues ε_i^{N+} then are given by

$$\varepsilon_i^{N+} = \varepsilon_i[v + v_H + \bar{v}_{xc}] + \Delta_{xc}^{N+}[\bar{v}_{xc}] = \varepsilon_i[\bar{v}_s] + \Delta_{xc}^{N+}[\bar{v}_{xc}]\,. \tag{18}$$

Eq. (18) again yields the same adjusted eigenvalues ε_i^{N+} for all members of the set $\bar{v}_{xc}$. That means the adjusted eigenvalues ε_i^{N+}, like the eigenvalues ε_i^{N-}, are uniquely defined.

For the LUMO eigenvalue we obtain

$$\begin{aligned}\varepsilon_{LUMO}^{N+} &= \varepsilon_{LUMO}[v + v_H + \bar{v}_{xc}] + \Delta_{xc}^{N+}[\bar{v}_{xc}] \\ &= \varepsilon_{LUMO}[v + v_H + \bar{v}_{xc}] + E_0^{N+1} - E_0^N - \varepsilon_{LUMO}[v + v_H + \bar{v}_{xc}] \\ &= E_0^{N+1} - E_0^N \end{aligned} \tag{19}$$

with Eq. (13) for $\Delta_{xc}^{N+}[\bar{v}_{xc}]$. This means the LUMO eigenvalue equals the negative of first electron affinity given by $E_0^{N+1} - E_0^N$ as it should. In the case of LDA or GGA functionals the negative of the adjusted LUMO eigenvalue, equals the first electron affinity calculated by a ΔSCF calculation with the LDA or GGA functional. Analogously to the case of ionization, this means Eq. (19) holds true not only for the exact functional but also for LDA or GGA functionals provided the exchange-correlation potentials and subsequently the KS eigenvalues are correctly adjusted energetically. It suggests itself to approximate higher electron affinities by the negatives of energetically higher KS eigenvalues ε_i^{N+}.

In summary, two KS eigenvalues spectra containing the eigenvalues ε_i^{N-} and ε_i^{N+}, respectively are associated with an electronic system. The first spectrum containing the eigenvalues ε_i^{N-} is related to ionization, the second one containing the eigenvalues ε_i^{N+} is related to the attachment of additional electrons. From the first spectrum the eigenvalues of the occupied orbitals have physical meaning, from the second spectrum the eigenvalues of the unoccupied orbitals are physically meaningful. By combining the eigenvalues of the occupied orbitals of the first spectrum with the eigenvalues of the unoccupied orbitals of the second spectrum an approximate quasiparticle spectrum ist obtained. The HOMO and LUMO eigenvalues of this combined spectrum are exact quasiparticle energies, that is they yield the exact first ionization potential and electron affinity. All other eigenvalues of this combined spectrum can be interpreted as approximate quasiparticle energies. The fact that two KS eigenvalue spectra are associated with an electronic system that need to be combined for an approximate quasiparticle spectrum follows from the basic ensemble KS formalism, more precisely from the presence of the derivative discontinuity of the exchange-correlation potential. By correctly adjusting energetically LDA and GGA exchange-correlation potentials also these approximate functionals exhibit a derivative discontinuity for finite systems and therefore lead to two KS eigenvalue spectra that can be combined to an approximate quasiparticle spectrum.

IV. IONIZATION POTENTIALS OF SMALL AND MEDIUM SIZE MOLECULES

V. CONCLUSIONS

Acknowledgements

This work was supported by the DFG through the Cluster of Excellence “Engineering of Advanced Materials” (www.eam.uni-erlangen.de) at the Friedrich-Alexander-Universität Erlangen-Nürnberg.

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