Exact exchange-correlation potentials for calculating the fundamental gap with a fixed number of electrons

M. J. P. Hodgson,1,2 J. Wetherell,3,4 and Emmanuel Fromager4

1Department of Physics, Durham University, South Road, Durham, DH1 3LE, United Kingdom
2European Theoretical Spectroscopy Facility
3LSI, École Polytechnique, CNRS, Institut Polytechnique de Paris, F-97728 Palaiseau
4Laboratoire de Chimie Quantique, Institut de Chimie, CNRS / Université de Strasbourg, 4 rue Blaise Pascal, 67000 Strasbourg, France

Capturing the discontinuous shift by \( \Delta \) in the exact exchange-correlation (xc) potential is the standard proposal for calculating the fundamental gap, \( E_g \), from the Kohn-Sham (KS) gap, \( \varepsilon_g \), within KS density functional theory (DFT), as \( E_g = \varepsilon_g + \Delta \), yet this discontinuity is absent from existing approximations. The ‘\( N \)-centered’ formulation of ensemble DFT artificially maintains a total electron number, \( N \), in order to yield \( E_g \) not through a discontinuous shift in the xc potential but via the ensemble-weight derivative of the xc energy. Within the \( N \)-centered approach we calculate exact xc potentials for a one-dimensional finite system and show analytically that \( \Delta \) can in fact be interpreted as a discontinuous shift in the exact \( N \)-centered ensemble xc potential, thereby extending to charged excitations an exact property of uncharged excitations. We show that applying the Levy-Zahariev ‘shift-in-potential’ procedure in this context relocates the discontinuous shift to the unimportant periphery of the system, so that the exact xc potential in effect is free of discontinuities and thus the inability of a local functional to capture discontinuous behavior is inconsequential.

I. INTRODUCTION

Kohn-Sham [1] (KS) density functional theory [2] (DFT) owes its success to its approximations, which achieve an unprecedented balance of computational efficiency and accuracy for electronic structure properties [3][10]. However, these approximations are notoriously unreliable for predicting the fundamental gap [11][12]. As such, computationally expensive methods outside of KS theory must be employed in conjunction with a KS calculation to correct the prediction of the gap, e.g., hybrid density functionals [13][28] or the GW approximation within many-body perturbation theory [29][34]. Calculating accurate gaps at the computational cost of a single KS calculation [35][39] offers the prospect of improved semiconductor, thermoelectric material [10][40][42] and photovoltaic [43][45] modeling.

In principle, KS DFT can yield the exact fundamental gap; in practice the exact xc energy of DFT and the corresponding xc potential of KS theory possess discontinuous features which have a strong nonlocal dependence on the electron density [2][14][52] and hence are difficult to capture in approximate functionals [11][35][58]. Perdew, Parr, Levy, and Balduz (PPLB) [46] proposed to calculate the gap – the ionization potential (IP), \( I \), minus the electron affinity (EA), \( A \) – within KS theory via the discontinuous constant shift, \( \Delta \), in the multiplicative xc potential, \( v_{xc}(r) \), which occurs as the electron number, \( N \), infinitesimally surpasses an integer [46][59], \( N \), where

\[
\Delta = \lim_{\delta \to 0^+} \left( v_{xc}(r)\big|_{N=N+\delta} - v_{xc}(r)\big|_{N=N-\delta} \right) = I - A - \varepsilon_{N+1} + \varepsilon_N, \tag{1}
\]

\( \varepsilon_N \) is the KS highest occupied molecular orbital (HOMO) energy and \( \varepsilon_{N+1} \) is the KS lowest unoccupied molecular orbital (LUMO) energy, both of the \( N \)-electron system. \( \Delta \), usually termed the ‘derivative discontinuity’, connects the fundamental gap to the KS gap, \( \varepsilon_{N+1} - \varepsilon_N \). However, common density-functional approximations based on the local or semi-local density are unable to capture the discontinuous shift in the xc potential when the electron number infinitesimally surpasses an integer and hence do not yield \( \Delta \) [60][61].

Senjean and Fromager defined an ‘\( N \)-centered’ KS system from which the exact fundamental gap can be calculated in principle [62][63]. Within their auxiliary system the electron number is fixed and integer with the purpose of calculating the system’s fundamental gap from the derivative (at \( \text{fixed} \) density) of the corresponding \( N \)-centered ensemble xc energy with respect to the ensemble weight rather than from a discontinuous shift in the xc potential. The theory was designed so that the exact xc potential does not have to shift discontinuously in order to yield the gap and hence commonly used approximations to the xc energy, such as the local density approximation (LDA), could in principle be employed reliably within the \( N \)-centered approach.

In this paper we study the exact \( N \)-centered approach: We calculate the exact ensemble xc energy as a function of the ensemble weight and the corresponding exact xc potentials for a one-dimensional finite model system for which the many-body Schrödinger equation can be solved exactly. We demonstrate both numerically and analytically that, when the exact ensemble xc potential is (arbi-
FIG. 1. PPLB case: (Top) The change in the KS potential upon the addition of δ electrons to the system; as δ → 0⁺ the change tends to a uniform shift of height Δ (numerical noise on the far right []). (Bottom) The 2-electron KS system to which δ electrons is added.

a We assume each xc potential decays |x| → ∞ = 0 without modeling an infinitely large system.

trarily) forced to asymptotically approach zero infinitely far from the center of the system, it experiences discontinuous shifts in the region of central density. They manifest as plateaus, just like in the PPLB approach. We also show how the exact Levy-Zahariev (LZ) shift relocates the discontinuous shift in the N-centered ensemble xc potential from the vicinity of the electron density to a region of space infinitely far from the center of the system, even as the ensemble weight (ξ) becomes infinitesimal.

II. PERDEW, PARR, LEVY, AND BALDУZ

First we study the PPLB approach in the absence of approximation: Employing our iDEA code [65], we calculate the exact KS potential, vN(x), of the N- and (N + δ)-electron systems as δ → 0⁺ to observe the shift Δ. We model a 1D atom with the external potential vext(x) = 3/(|x| + 1) and N = 2 exactly (both electrons have the same spin). The exact ensemble many-body density is given by

\[ n^\delta(x) = (1 - \delta)n_N(x) + \delta n_{N+1}(x), \]

where n_i(x) is the many-body density of the i-electron system. From n^\delta(x) we reverse-engineer the KS equations to find the corresponding exact xc potential and KS energies.

We calculate the exact IP and EA via many-body total energy differences of the N-, (N+1)- and (N−1)-electron many-body systems. Employing the exact KS energies of the N-electron KS system, we calculate the exact Δ via Eq. [1]. Figure [1] shows that as δ → 0⁺ the change in the KS potential (v_N^\delta(x) − v_N^\delta(x)) tends to a uniform constant of magnitude Δ [52] [66]. In this case the N-electron KS potential is defined such that v_N^\delta(|x| → ∞) = 0. v_N^\delta(x) possess a discontinuous shift which elevates the potential in the central region of the system. Note that as the plateau tends to a uniform constant shift, the KS potential still asymptotically approaches zero infinitely far from the center of the system; as discussed in Refs. [52] and [66].

This discontinuous behavior is difficult to capture in an approximate density functional and hence in practice the PPLB approach is not used.

III. N-CENTERED ENSEMBLE APPROACH

We now turn to the N-centered approach. Following Ref. [62] we start from the general two-weight formulation of N-centered ensemble DFT where the ensemble density is

\[ n_{\xi}(x) = \left[ 1 - \xi N - \frac{1}{N} - \xi N + \frac{1}{N} \right] n_N(x) + \xi n_{N-1}(x) + 1 \]

(2)

By analogy with Ref. [63] we will refer to the special cases \{ξ−, 0\} and \{0, ξ+\} as left and right N-centered ensembles, respectively. For brevity we adopt the notation \{ξ−, 0\} ≡ ξ−, \{0, ξ+\} ≡ ξ+, and \{ξ, ξ\} ≡ ξ. Below we consider the left and then the right ensemble, for which we vary the ensemble weights as such: When ξ− = 0, 0 ≤ ξ− ≤ N−1, and when ξ+ = 0, 0 ≤ ξ+ ≤ N+1.

The ensemble energy is

\[ E_{\xi}(\xi, N) = \left[ 1 - \xi N - \frac{1}{N} - \xi N + \frac{1}{N} \right] E_N + \xi E_{N-1} + E_{N+1}. \]

(3)

The IP and EA can be extracted separately from the ensemble energy by differentiating with respect to ξ− and ξ+; see Eqs. 1 and 10. The ensemble energy, E(ξ−, ξ+), is a functional of the ensemble density n_{\xi}(x) which, unlike the PPLB approach, integrates to the fixed (‘central’) integral number of electrons, N. This many-body density is exactly reproduced by the non-interacting KS system:

\[ n_{\xi}(\xi, N) = \left( 1 - \xi N - \frac{1}{N} - \xi N + \frac{1}{N} \right) \sum_{i=1}^{N} | \phi_i^{\xi}(x) |^2 \]

(4)

where \{ϕ_i^{\xi}(x)\} are the set of ensemble KS orbitals. As within the regular KS DFT approach, the auxiliary KS system employs the Hartree-xxc (Hxc) potential, the functional derivative of the ensemble Hxc en-
ergy $E_{\text{Hxc}}^{(\xi_-^\pm)}[n]$, to ensure that the non-interacting system yields the exact many-body ensemble density, where

$$E_{\text{Hxc}}^{(\xi_-^\pm)}[n] = E_{\text{H}}[n] + E_{\text{xc}}^{(\xi_-^\pm)}[n],$$

and $E_{\text{H}}[n]$ is the conventional (weight-independent) Hartree functional. This formally exact deconstruction may not be optimal for approximate functionals as ghost-interaction errors $[67–69]$ may be introduced. Alternatively one may use exact (orbital-dependent) expressions for both Hartree and exchange ensemble energies $[70, 71]$ or opt for an alternative weight-dependent definition of the ensemble Hartree energy $[72]$. In this paper we mainly focus on the exact N-centered approach; for our LDA calculations we employ this deconstruction.

By design, the N-centered ensemble density integrates to $N$, which is fixed with the aim of conveniently expressing $\Delta = I - A - \varepsilon_{N+1} + \varepsilon_N$ as a weight derivative where the ensemble density is held constant $[62, 63]$, as such

$$\Delta = \left[ \frac{\partial E_{\text{xc}}^{\varepsilon_n}}{\partial \varepsilon_-} \right]_{\xi_- = 0} + \left[ \frac{\partial E_{\text{xc}}^{\varepsilon_n}}{\partial \varepsilon_+} \right]_{\xi_+ = 0} n = n_N$$

$$\equiv \frac{\partial E_{\text{xc}}^{\varepsilon_n}}{\partial \varepsilon_-} \bigg|_{\xi = 0, n = n_N}.$$

In Sec. XIV we show analytically that $\Delta$ can also be interpreted, in the context of N-centered ensemble DFT, as a derivative discontinuity, exactly like in the PPLB approach.

### A. Calculating the ionization potential

#### 1. Exact theory

We start from the general expression of the IP for an $N$-electron system within the N-centered approach – Eq. (33) in Ref. 62. By considering the left $N$-centered ensemble we obtain

$$I = -\varepsilon_N^\xi_- + \left[ \frac{\xi_-}{N} + 1 \right] \frac{\partial E_{\text{xc}}^{\varepsilon_n}}{\partial \varepsilon_-} - C\varepsilon_-[n] \bigg|_{n=n_-^\xi}, \quad (5)$$

where $C\varepsilon_-[n]$ is the analog of the LZ shift in potential for $N$-centered ensembles $[64]$. The general two-weight expression for which is

$$C^{(\xi_-^\pm)}[n] = E_{\text{Hxc}}^{(\xi_-^\pm)}[n] - \int dx \ n(x) \ E_{\text{Hxc}}^{(\xi_-^\pm)}[n](x),$$

We stress that, unlike in the conventional PPLB approach, the HOMO and LUMO energies ($\varepsilon_N^\xi_-^+$ and $\varepsilon_{N+1}^\xi_-$, respectively) are defined up to an additive constant. This is connected to the fact that the left and right $N$-centered ensemble densities ($n^-\xi_-$ and $n^+\xi_+$, respectively) integrate to the (fixed and integer) central number of electrons, $N$. On the other hand, the LZ-shifted energies, $\varepsilon_N^\xi_-^+$ = $\varepsilon_N^\xi_- + C\varepsilon_-[n] \big|_{n=n_-^\xi}$ and $\varepsilon_{N+1}^\xi_+ = \varepsilon_N^\xi_+ + C\varepsilon_-[n] \big|_{n=n_+^\xi}$, are truly unique and independent of any overall shift in the potential.

We study the same 1D atom of Sec. II but now the electron number is fixed at $N = 2$ within the N-centered approach. First we compare the exact IP to that of Eq. (6).

We calculate the exact many-body ensemble density via Eq. (2) considering only the left contribution and employing the exact many-body density for the $N$- and $(N-1)$-electron systems. We then employ the ensemble density, $n^\xi_-(x)$, and reverse-engineer the KS equations to find the exact ensemble xc potential and KS energies. Our results are shown in Fig. 2. We choose the ensemble KS potential that tends to zero as $|x| \rightarrow \infty$.

With this choice of KS potential we find that for $0 \leq \xi_- < \frac{N}{N-1}$, $I = -\varepsilon_N^\xi_-$ and hence

$$\left( \frac{\xi_-}{N} + 1 \right) \frac{\partial E_{\text{xc}}^{\varepsilon_n}}{\partial \varepsilon_-} \bigg|_{n=n_-^\xi} = C\varepsilon_-[n] \big|_{n=n_-^\xi}. \quad (7)$$

This can be proven analytically, as follows: For $0 \leq \xi_- < \frac{N}{N-1}$ the $n_N(x)$ term dominates the asymptotic decay of the density (Eq. (2)) far from the center of the system:

$$\lim_{|x| \rightarrow \infty} n_{\xi^-}(x) = \left( 1 - \frac{N-1}{N} \xi_- \right) n_N(x) \propto e^{-2\sqrt{2|\xi_-|/x}}. \quad (8)$$

In addition, in the asymptotic region, the KS orbital with the highest energy ($\varepsilon_N^\xi_-$) will dominate the KS density (Eq. (4)):

$$\lim_{|x| \rightarrow \infty} n_{\xi^{-}}(x) = \left( 1 - \frac{N-1}{N} \xi_- \right) |\phi_{\varepsilon_N^\xi}^\xi_-(x)|^2 \propto e^{-2\sqrt{2\xi_-/|x|}},$$

as, by design, $\phi_{\varepsilon_N^\xi}^\xi_-(x) \rightarrow 0$. Hence, as this exponential decay equals that of Eq. (8) by definition, $I = -\varepsilon_N^\xi_-$ and from Eq. (5), Eq. (7) must follow.

We now examine $\varepsilon_{\text{xc}}^\xi_-(n_{\xi^-})(x) \equiv \varepsilon_{\text{xc}}^\xi_-(x) + C\varepsilon_-[n] \big|_{n=n_-^\xi} \bigg|_{\xi_- = \frac{N}{N-1}}$, as $\xi_- \rightarrow 2^{-} \bigg( \frac{N}{N-1} = 2 \bigg)$, which is the fully ionized limit, i.e., $n_{\xi^-} \rightarrow n_N$, see if there is any discontinuity in the exact xc potential.

Figure 3 (Top) shows that with the LZ shift there is no plateau which yields a discontinuous shift in the xc potential in the region of the atom and hence approximate functionals which do not capture such discontinuities could be employed as reliable approximations to $\varepsilon_{\text{xc}}^\xi_-(x) + C\varepsilon_-[n] \big|_{n=n_-^\xi}$, unlike within the PPLB approach. On the other hand, Fig. 4 (Middle) shows $\varepsilon_{\text{xc}}^\xi_-$ which contains a plateau similar to that of Fig. 1. The LZ shift ‘relocates’ the discontinuity from the centralized region to the edges of the system – a region with little influence on the system’s properties $[73]$. As $\xi_- \rightarrow 2^{-}$,
from the exact xc potential, one requires a reliable approximation to the ensemble-weight dependence in the xc energy within the N-centered approach.

2. The local density approximation

Next we calculate the IP within the N-centered approach employing the LDA to the xc energy, which neglects the weight dependence entirely. Our LDA to the xc energy was parameterized from the 1D homogeneous electron gas [74]. The LDA does not capture PPLB’s discontinuous shift, , in the xc potential. Therefore, although it is unsuitable for predicting the gap within the PPLB approach, it can be employed within the N-centered approach.

Figure 4 shows the prediction for the IP evaluated via Eq. (5) within the LDA. is comparable to the exact LZ-shifted HOMO KS energy. Therefore, if an accurate approximation to the weight derivative of the xc energy were introduced, the LDA could yield a reliable prediction for . This highlights the importance of developing reliable approximations to the xc energy which account for the ensemble-weight dependence [70, 73].

We see in Fig. 4 that the LDA reproduces the LZ-shifted HOMO energy well, especially when . However, Fig. 5 shows that when , the LDA LZ-shifted xc potential is inaccurate, including the LDA LZ shift. This is likely because for this LDA is employed for an ensemble well beyond the ground state systems from which it was parameterized. Despite this the error in the LDA LZ-shifted HOMO energy is acceptable owing to a cancellation errors among the approximate xc energy (which contributes to the LZ shift) and the LZ-shifted potential which is overestimated in the region of
the atom and underestimated away from it.

B. Calculating the electron affinity

1. Exact theory

We now turn to the EA. We employ the right ensemble system for which \( \xi^+ \) is the ensemble weight; see Eq. (2). The exact EA for the \( N \)-electron many-body system is given by the following expression \[ 62 \]:

\[
A = -\varepsilon_{N+1}^{\xi^+} + \left[ \frac{\xi^+}{N} - 1 \right] \frac{\partial E_{xc}^{\xi^+}[n]}{\partial \xi^+} - C^{\xi^+}[n] \bigg|_{N=n_{\xi^+}}.
\]

We model the same 1D atom as above. As before, we calculate the exact many-body ensemble density via Eq. (2) employing the exact many-body density for the \( N \)- and \((N+1)\)-electron systems. We then employ \( n^{\xi^+}(x) \) and reverse-engineer the KS equations to find the exact ensemble xc potential and KS energies. Our results are shown in Fig. 6 [23]: We compare our calculated EA to the exact obtained via total energy differences of the \( N \)- and \((N+1)\)-electron systems. Recall that, as before, we (arbitrarily) choose a KS potential, \( v_{\xi^+}^{xc}(x) \), that asymptotically approaches 0 towards infinity. Note that the expression on the right-hand side of Eq. (9) is invariant under a constant shift in the KS potential, by design.

Like for the IP, \( \varepsilon_{N+1}^{\xi^+} \) is found to be independent of \( \xi^+ \) for \( 0 < \xi^+ < \frac{N}{N+1} \). This is because the exact many-body ensemble density decays as

\[
\lim_{|x| \to \infty} n^{\xi^+}(x) = \xi^+ n_{N+1}(x) \propto e^{-2\sqrt{x^2|x|}}
\]

far from the center of the system for \( 0 < \xi^+ < \frac{N}{N+1} \). In this asymptotic region, the KS orbital with the highest energy \( (\varepsilon_{N+1}^{\xi^+}) \) dominates the KS density provided \( \xi^+ > 0 \), and hence

\[
\lim_{|x| \to \infty} n^{\xi^+}(x) = \xi^+ \left| \phi_{N+1}^{\xi^+}(x) \right|^2 \propto e^{-2\sqrt{-2\varepsilon_{N+1}^{\xi^+}|x|}}.
\]

Therefore, as the many-body ensemble density and the KS density are the same, \( A = -\varepsilon_{N+1}^{\xi^+} \)

\[
\left( \frac{\xi^+}{N} + 1 \right) \frac{\partial E_{xc}^{\xi^+}[n]}{\partial \xi^+} \Bigg|_{n=n_{\xi^+}} = C^{\xi^+}[n] \bigg|_{n=n_{\xi^+}},
\]

for \( 0 < \xi^+ < \frac{N}{N+1} \).

We now examine \( v_{\xi^+}^{xc} \) and \( v_{\xi^+}^{xc} + C^{\xi^+}[n] \big|_{n=n_{\xi^+}} \) as \( \xi^+ \to 0^+ \) to observe if in this case there is a discontinuous shift in the potential. As for the IP in Sec. III A, we observe no shift in the potential in the region of the centralized electron density when the LZ shift is included, as expected [23]; see Fig. 7 (Top). Instead the shift occurs in the outer region of the atom and as \( \xi^+ \to 0^+ \) the steps we see in Fig. 7 (Top) approach an infinite distance from the atom. Without the LZ shift we observe a shift in the potential in the vicinity of the atom (Fig. 7 (Middle)), as for the IP case above. In this case it can be shown that the height of the steps equals \( \Delta \) as \( \xi^+ \to 0^+ \); see Sec. IV

2. The local density approximation

Figure 8 shows the LDA’s prediction for the EA. Once again it is clear that the ensemble-weight dependence is important for the EA prediction within the \( N \)-centered system; see Sec. III A 2.

As for the IP, the LDA yields an accurate LZ-shifted KS energy for \( \xi^+ < 0.5 \); see Fig. 8 Figure 9 shows that
There is a discontinuous shift in the potential as $\xi_+ \to 0^+$ (numerical noise on the far right). (Middle) The exact xc potential. There is a discontinuous shift in the potential as $\xi_+ \to 0^+$. (Bottom) The density and xc potential for $\xi_+ = 0$. We choose $\psi_+^N(x)$ to asymptotically approach 0.

For both the left and the right ensemble systems as $\xi \to 0$ the LDA LZ-shifted KS energies are reliable approximations to the exact LZ-shifted KS energies for the $N$-electron system owing to a cancellation of errors between the LDA KS energies and the LDA LZ shift; see Figs. 4, 5 and 8. Further investigation is required to determine whether this cancellation of errors occurs for other types of system. These results imply that with an accurate local approximation to the ensemble-weight derivative of the xc energy, in the spirit of previous works on neutral excitations \cite{77, 78}, the N-centered approach within the LDA could yield accurate fundamental gaps for a low computational cost.

IV. ‘LEFT-TO-RIGHT’ DISCONTINUOUS SHIFT IN THE N-CENTERED EXCHANGE-CORRELATION POTENTIAL

In the original formulation of $N$-centered ensemble DFT \cite{02}, it was emphasized that modeling derivative discontinuities in order to recover the fundamental gap from the KS gap is unnecessary. Instead, one should focus on the weight dependence of the ensemble xc energy. Still, in the light of our numerical results and by analogy with Gross-Oliveira-Kohn DFT \cite{70, 75} for neutral excitations, one may wonder if a clear and formal connection can be established between weight derivatives and derivative discontinuities in the context of $N$-centered ensemble DFT. Below we establish this connection.

The asymptotic behavior of the left and right $N$-centered ensemble densities revealed that $I = -\left(\xi_N^L - v_{xc}^L (|x| \to \infty)\right)$, for $0 \leq \xi_- < \frac{N}{N-1}$, and $A = -\left(\xi_{N+1}^L - v_{xc}^L (|x| \to \infty)\right)$, for $0 < \xi_+ \leq \frac{N}{N-1}$. In the PPLB approach, the xc potential tends to zero infinitely far from the center of the system, as a consequence of Janak’s theorem. In the $N$-centered picture, the potential is unique up to a constant. If we make the (arbitrary)
choice that the $N$-centered ensemble xc potential always tends to zero at infinite distance,

$$
v_{xc}^\xi ([x] \to \infty) = v_{xc}^\xi ([x] \to \infty) = 0, \quad (10)
$$

then the LZ shift and weight derivative contributions to the IP/EA compensate each other exactly (shown above), which can be written more explicitly as follows:

$$
E_{\text{Hxc}}^{\xi \pm} [n^{\xi \pm}] - \int dx \, v_{Hxc}^{\xi \pm} (x) n^{\xi \pm} (x) = (\xi_ \pm + N) \frac{\partial E_{\text{xc}}^{\xi \pm} [n]}{\partial \xi_ \pm} \bigg|_{n=n^{\xi \pm}}. \quad (11)
$$

Note that, with the constraint in Eq. (10), $v_{xc}^{\xi_+ = 0} (x)$.

In summary, if we force the $N$-centered ensemble xc potential to asymptotically approach zero, we recover IP/EA theorems which are formally identical to those derived in PPLB. In this case, the exact KS HOMO and LUMO energies are weight-independent and

$$
I - A = \varepsilon_{N+1}^{\xi_+ - \xi_0} - \varepsilon_N^{\xi_0} = \varepsilon_{N+1}^{\xi_+ - \xi_0} - \varepsilon_N^{\xi_0} = \varepsilon_{N+1}^{\xi_+ = 0} + v_{xc}^{\xi_+ \to 0^+} (x) - v_{xc}^{\xi_+ = 0} (x) - \varepsilon_N^{\xi_+ = 0} = \varepsilon_{N+1} - \varepsilon_N + \Delta. \quad (14)
$$

V. CONCLUSION

The ‘$N$-centered’ system corresponds to an ensemble Kohn-Sham (KS) system in which the electron number is fixed and integer, which permits the fundamental gap to be calculated from the KS gap, not through the usually unattainable ‘derivative discontinuity’, $\Delta$, which manifests in the exact exchange-correlation (xc) potential as a discontinuous shift within the usual Perdew, Parr, Levy, and Baldiz (PPLB) approach \[16\] to calculating the fundamental gap, but instead via the ensemble-weight derivative of the $N$-centered xc energy.

We modeled the $N$-centered system exactly in 1D in order to study the exact xc energy and corresponding xc potential as a function of the ensemble weight ($\xi$). We found that the xc potential can always be (arbitrarily) forced to asymptotically approach zero infinitely far from the center of the system. We employed this constraint to prove analytically that $\Delta$ manifests within the exact xc potential of the $N$-centered ensemble as a derivative discontinuity, thus extending to charged excitations Levy’s exact property of number-conserving excitations \[79\]. We
demonstrated numerically and analytically that the exact Levy-Zahariev (LZ) shift ‘relocates’ this discontinuity to the periphery of the system – a region with negligible importance to the system’s observable properties.

We employed a standard 1D local density approximation (LDA) to the xc energy which completely neglects the ensemble weight dependence. We found, for our prototype system, that the LDA LZ-shifted KS energies were accurate for a significant range of ensemble weights including $\xi = 0$ which corresponds to the regular $N$-electron KS system.

Within the PPLB perspective the LDA is unreliable because it does not exhibit the required discontinuous shift in the xc potential and hence predicting the electron affinity (EA) results in a substantial error. Additionally, the LDA yields an inaccurate ionization potential (IP) because it does not exhibit the required discontinuous shift in the xc potential and hence predicting the electron affinity which completely neglects the ensemble weight dependence. We found, for our prototype system, that the LDA LZ-shifted KS energies were accurate for a significant range of ensemble weights including $\xi = 0$ which corresponds to the regular $N$-electron KS system.

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