

Polarizabilities of Polyacetylene from a Field-Counteracting Semilocal Functional

A. Karolewski, R. Armiento, and S. Kümmel*

Physics Institute, University of Bayreuth, D-95445 Bayreuth, Germany

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Abstract: Predicting the polarizabilities of extended conjugated molecules with semilocal functionals has been a long-standing problem in density functional theory. These difficulties are due to the absence of a term in the typical semilocal Kohn–Sham exchange potentials that has been named “ultranonlocal”. Such a term should develop in extended systems when an external electric field is applied, and it should counteract the field. We calculate the polarizabilities of polyacetylene molecules using the recently developed extended Becke–Johnson functional. Our results show that this functional predicts the polarizabilities with much better accuracy than typical semilocal functionals. Thus, the field-counteracting term in this functional, which is semilocal in the Kohn–Sham orbitals, can realistically describe real molecules. We discuss approaches of constructing an energy functional that corresponds to this potential functional, for example, via the Levy–Perdew virial relation.

1. Introduction: Step Structures in the Kohn–Sham Potential

The enormous success of density functional theory (DFT) in solid-state physics and molecular chemistry to a considerable extent has been due to the remarkable balance between accuracy and computational cost which (semi)local functionals like the local density approximation and generalized gradient approximations provide. Yet, the developers of some of the most reliable semilocal functionals themselves pointed out¹ a feature of the exact exchange–correlation potential of Kohn–Sham density functional theory that none of the standard semilocal functionals has: the exact potential is discontinuous as a function of the particle number. This “derivative discontinuity” feature of Kohn–Sham theory has found considerable attention over the years, with refs 2–5 being just a few examples from a body of literature that is far too vast to cite in completeness. The derivative discontinuity of ground-state density functional theory in the solid-state context is prominently related to the band gap question, see, for example, refs 2 and 6–8. In molecular physics, it is related to at least two frequently encountered problems.

As was already pointed out in ref 1, it is only due to the derivative discontinuity that Kohn–Sham theory can lead

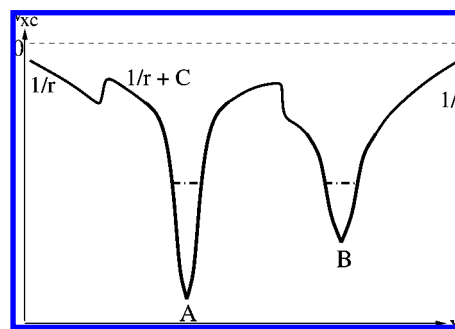


Figure 1. Schematic depiction of the exact v_{xc} for a system of two different atoms at a very large separation (arbitrary units). The dashed–dotted lines indicate the energies of the Kohn–Sham eigenvalues discussed in the main text. To the left of A, the potential first tends to a positive constant C and then steps down to fall off to 0 like $1/r$.

to neutral fragments when a molecule dissociates. The spatial features which the exact Kohn–Sham exchange–correlation potential develops in order to enforce this “principle of integer preference”⁹ are schematically depicted in Figure 1. When two different atoms, A and B, with A having a larger electronegativity than B, are considered as being rigorously disconnected, the highest occupied eigenvalue of A is more negative than the one of B. When the same two atoms are close to each other and form a diatomic molecule, the

* Corresponding author e-mail: Stephan.Kuettel@uni-bayreuth.de.

eigenvalues of the molecule in general will be different from the eigenvalues of the separate atoms, reflecting the charge redistribution that is associated with the electronic bond. However, now consider the situation that the distance between the two atoms forming the molecule is steadily increased to large values, that is, one is looking at a stretched diatomic molecule A–B. If the interatomic distance is extremely large, for example, on the scale of meters, then this “extremely stretched diatomic molecule” will show the same physical properties as two separate neutral atoms. Therefore, one may be tempted to think that the Kohn–Sham eigenvalues one finds for the stretched diatomic molecule are the same as the ones for the two isolated atoms. But this is not the case for the ultimate, exact density functional: When the two atoms, A and B, are considered as one very extended system, a steplike structure develops in ν_{xc} , and due to this step, the Kohn–Sham potential of the stretched molecule is not simply the sum of the two Kohn–Sham potentials of two isolated atoms. In the stretched molecule, the step in ν_{xc} “lifts up” the potential well of A, nearly aligning the eigenvalues which would be the highest occupied eigenvalues of A and B if the atoms were rigorously isolated. At any very large but finite separation, one eigenvalue in the stretched diatomic will be infinitesimally higher in energy than the other, and its corresponding orbital will be mostly localized around atom B. When the interatomic distance tends to infinity, the eigenvalues become degenerate.

The exact ν_{xc} of the very stretched diatomic molecule is schematically depicted in Figure 1, with the dashed–dotted lines indicating the energies of the just discussed two eigenvalues. The eigenvalue difference becomes smaller as the distance between A and B becomes larger. Also, with increasing distance, the steps in ν_{xc} become sharper, and the down-step of ν_{xc} to the left of A, which occurs in the region of space where the density starts to be dominated by the highest occupied orbital, moves farther to the left. Potentials that are reconstructed from accurate densities show features similar to the ones just described.^{10,11} But the ν_{xc} of a standard semilocal density functional does not at all show the step structure. Therefore, such functionals typically lead to fractionally charged dissociation fragments.¹²

To date, step structures in the correlation potential are not incorporated in any of the typical density functional approximations. Functionals showing them have been constructed¹³ but are involved to compute and typically rely on reconstructions from ensemble densities.^{11,14} For exchange, however, the situation is more transparent. Due to the fact that the expression for the Kohn–Sham exchange functional is known in terms of the Kohn–Sham orbitals, the step structure in the Kohn–Sham exchange potential can be understood analytically. It has been discussed in detail, for example, by Krieger et al.,^{3,15} with the exchange potential “step structure” being closely related to orbital overlap or occupation of a new orbital upon the addition of an extra electron.^{6,16,8} Several approximations showing such steps have been developed.^{3,17–19,32}

The step structure features of ν_{xc} are related to a second nontrivial problem. Long-range charge transfer is not well described by standard semilocal functionals.²⁰ This issue

manifests very prominently in the well-known fact that the static electric polarizabilities of extended molecular systems are seriously overestimated by semilocal functionals.²¹ This failure is due to the fact that the exact exchange potential of an extended molecular system develops a term which counteracts an externally applied electric field that polarizes the system,²² but this term is missing in the semilocal approximations.

The problem of correctly describing the electrical response of conjugated polymers is of great practical interest because of the widespread use that these materials find in optoelectronic applications. So far, the only density functionals that yield a proper field-counteracting term were exact-exchange,^{22–24} range-separated^{25,26} or other²⁷ functionals using exact exchange, or self-interaction corrected functionals.^{28–30} Compared to semilocal approaches, these functionals are associated with a considerably increased computational burden stemming from having to evaluate many Coulomb integrals on the one hand and having to solve the optimized effective potential (OEP) equation on the other. (The latter statement applies to those approaches staying in the Kohn–Sham realm). Therefore, a computationally cheaper approach yielding a comparable accuracy is highly desirable.

Recently, Becke and Johnson³¹ showed that a simple expression which is semilocal in the Kohn–Sham orbitals quite accurately reproduces the “step-structure features” of the exact exchange Kohn–Sham potential. Yet more recently, the expression proposed by Becke and Johnson has been extended to yield proper asymptotic behavior and behave consistently for systems in an external electric field.³² The extended Becke–Johnson (BJ) expression for the exchange potential of a system in an external electric field Fz is

$$\nu_x^{\text{BJ}}(\mathbf{r}) = \nu_x^{\text{h}}(\mathbf{r}) + \nu_x^{\text{corr}}(\mathbf{r}) \quad (1)$$

where we have dropped the spin index for ease of notation. Here, $\nu_x^{\text{h}}(\mathbf{r})$ is interpreted as an effective potential due to the exchange hole. Presently, the Slater potential is employed, but other, simpler choices can be made without a significant loss of accuracy.³¹ The second term, $\nu_x^{\text{corr}}(\mathbf{r})$, is a correction modeling the response part of the exact exchange potential. The steplike structures in the extended BJ expression are exclusively due to $\nu_x^{\text{corr}}(\mathbf{r})$. Explicitly, this term reads

$$\nu_x^{\text{corr}}(\mathbf{r}) = \frac{1}{\pi} \sqrt{\frac{5}{12}} \left(\sqrt{\frac{2\tau}{n}} - \sqrt{-2\epsilon_{\text{max}}} - \frac{Fz}{\sqrt{-2\epsilon_{\text{max}}}} \right) \quad (2)$$

(in Hartree atomic units), where $\tau = (1/2) \sum_{i_{\text{occ}}} |\nabla \varphi_i|^2$ is the noninteracting kinetic energy density computed from the occupied Kohn–Sham orbitals φ_i , n is the density, and ϵ_{max} denotes the highest-occupied Kohn–Sham eigenvalue.

It was shown³² that this potential shows a step structure which, as discussed in the context of Figure 1, is closely connected to the derivative discontinuity. It was also shown that it yields polarizabilities of small hydrogen chains with an accuracy comparable to that of exact exchange methods. These results showed that constructing approximations for ν_{xc} directly (instead of approximations for E_{xc}) is an attractive idea that may lead to an elegant and efficient solution of the

field-counteracting term problem. However, two important questions regarding this approach have remained open so far: First, how reliable are the conclusions that were drawn from the hydrogen chain results; that is, does the approach also work for real, existing conjugated molecules? In other words, did the simplicity of the hydrogen chain model lead to artificially good results? Second, can one construct an energy corresponding to this potential functional, for example, via the exchange virial relation?³³ The latter question is interesting also from the point of view of recent work which shed additional light on the BJ approach by showing that it is one of a whole class of potential approximations and used the exchange virial relation to construct energy expressions.³⁴

We address both of these questions in the following. In section 2, we report static electric dipole polarizabilities of acetylene oligomers. Our results show that the extended BJ expression yields polarizabilities that compare favorably with previously calculated exact exchange values. They also show that the extended BJ potential can lead to nonvanishing asymptotic constants, a feature known from the exact Kohn–Sham exchange potential. These findings solidify the relevance of the extended BJ potential and the idea of developing exchange-correlation *potential* functionals. In section 3, we demonstrate the problems of defining an energy corresponding to the model potential. We show that straightforwardly using the exchange virial relation is problematic, and we give ideas of how this problem may be addressed in future work.

2. Electric Response of Polyacetylene and the Effect of Orbital Nodal Surfaces

Polyacetylene has been the paradigm conjugated polymer of molecular electronics research efforts. As well, it has become the paradigm system for the failure of semilocal functionals to describe the electrical response of extended conjugated molecules. Therefore, calculating the static electric polarizabilities of polyacetylene units is an ideal test for the practical usefulness of the extended BJ potential functional. To the best of our knowledge, it is the first test for real conjugated systems and therefore important. The only previous test that we know of was for hydrogen chains.³² This previous test may thus not completely account for the complexity of a real molecule's electronic structure.

Our calculations are based on a fully numerical solution of the Kohn–Sham equations on a real space grid.^{32,35} We thus avoid possible problems due to basis set limitations in the polarizability calculations. The polarizabilities are obtained by a finite-field, finite-difference approach; that is, we calculate the electrical dipole moment along the molecular axis, μ , for several values of the applied electric field, F , and obtain $\alpha = d\mu/dF$ from finite differences. A general and more detailed description of this type of approach can be found, for example, in ref 36. The molecular geometry that we based our calculations on is the Hartree–Fock geometry schematically depicted in Figure 2. Our aim here is to assess the validity of a theoretical approach by comparison to reference work. Therefore, we chose the geometry that was used in earlier works.^{21,38–40}

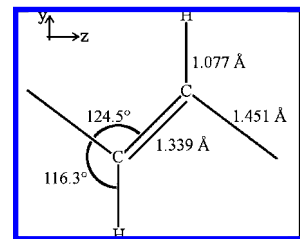


Figure 2. Sketch of the geometry that the polyacetylene calculations were based on. See main text for discussion.

Table 1. Longitudinal Static Electric Dipole Polarizabilities (in a_0^3) for Polyacetylene Units As Obtained from LDA, the Extended Becke–Johnson Functional, Hartree–Fock,³⁸ and Perturbation Theory (MP2) Calculations³⁹

	C ₄ H ₆	C ₆ H ₈	C ₈ H ₁₀	C ₁₀ H ₁₂	C ₁₂ H ₁₄	C ₁₄ H ₁₆
LDA	88	174	296	457	661	915
ext. BJ	70	134	224	338	480	649
HF	75	142	229	332	448	575
MP2	64	112	187	267	357	455

Table 1 compares the values for the longitudinal static electric polarizability that are obtained in the local density approximation³⁷ (LDA), the extended Becke–Johnson (ext. BJ) approach,³² unrestricted Hartree–Fock (HF),³⁸ and second-order Møller–Plesset perturbation theory (MP2).³⁹ Typical values obtained with generalized gradient approximation functionals are similar to LDA and therefore not given separately. Comparing the LDA polarizabilities (first row of Table 1) to the HF and MP2 ones (bottom rows) exemplifies the known serious overestimation of the response of conjugated systems that is obtained with semilocal density functionals.

So far, the standard interpretation of the BJ potential has been that it is an approximation to the exact Kohn–Sham exchange potential. In this spirit and in view of previous results indicating that Kohn–Sham exact exchange and HF exchange lead to very similar polarizabilities,²⁴ a reasonable comparison to make is the one between the extended BJ and the HF results. Looking at C₄H₆ to C₁₀H₁₂ in rows two and three of Table 1 gives a very positive impression in this respect. The values from the extended BJ functional are within roughly 5% of the HF values, slightly underestimating the HF result for the smallest systems and slightly overestimating for the large ones. This is a substantial improvement over the huge overestimation that one finds with LDA. For the two largest molecules that we studied, C₁₂H₁₄ and C₁₄H₁₆, the extended BJ potential still yields a substantial improvement over LDA, but the difference with respect to the HF results increases to 7% and 13%, respectively. Thus, the extended BJ potential in this respect behaves similarly²⁴ to the Krieger–Li–Iafrate (KLI) approximation.³ In view of the fact that the decisive ingredient in the BJ potential is a semilocal quantity,³¹ this quality, although not perfect, is without doubt an encouraging result.

A natural question is whether the reasonable polarizabilities of polyacetylene that one finds in the extended BJ approach can be traced back to a field-counteracting term like in the case of hydrogen chains and exact-exchange methods. In order to investigate this question, we have

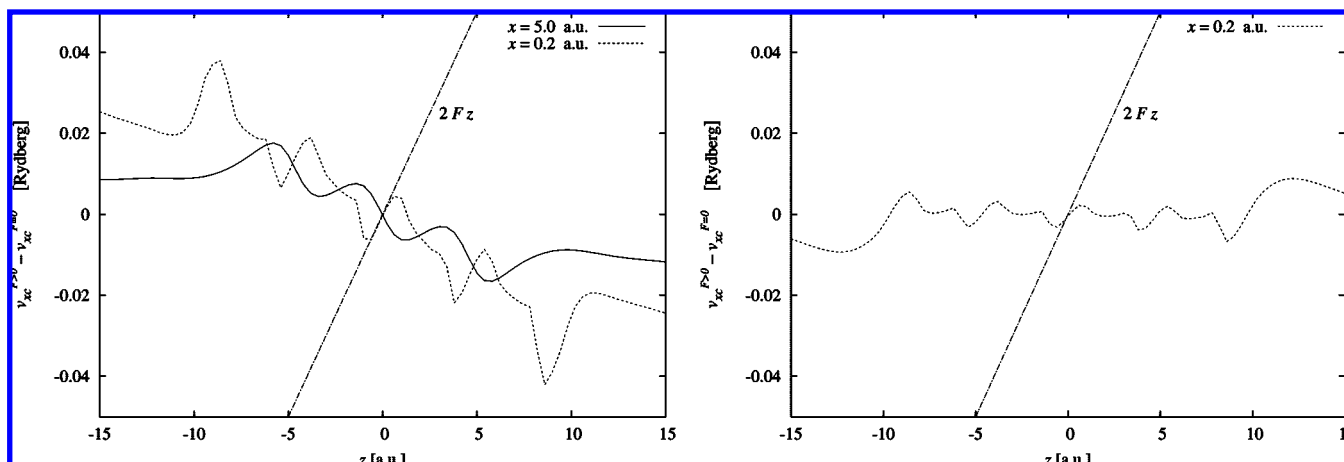


Figure 3. The difference between the exchange-correlation potentials with and without an externally applied electric field for C_8H_{10} (in atomic units). The molecule lies in the (y,z) plane. Left half: The full curve shows the v_{xc} difference along the line $(x = 5, y = 0, z)$. The dashed curve shows the v_{xc} difference along the line $(x = 0.2, y = 0, z)$, which is the z line closest to the molecular plane that lies exactly on our numerical grid. The straight dashed–dotted line indicates the external electric field. Note that the extended BJ potential counteracts the external field, as it should. Also note that the asymptotic behavior of the BJ v_{xc} difference depends on the distance to the molecular plane. Right half: The same difference shown for LDA along the line $(x = 0.2, y = 0, z)$. Note that the overall trend of LDA is with the external field.

followed the practice introduced in ref 22 and plotted the difference between the v_{xc} one finds along the molecular axis with an external electric field applied and the v_{xc} one finds without external field. The left half of Figure 3 shows this potential difference for the extended BJ approach, the right half for LDA. For the extended BJ potential, we show two plots. Each one is along a line running parallel to the molecular axis, which in our case lies in the z direction, compare Figure 2. The full curve shows the potential difference one finds at a distance of 5 au above the molecular plane. This curve looks reassuringly similar to what was found for the hydrogen chains in ref 32 and to what one may expect on the basis of earlier exact-exchange calculations: the exchange-correlation potential slopes against the external electric field (straight dashed–dotted line).

However, looking at the plot in the immediate vicinity of the molecular plane (dashed curve, $x = 0.2$ au) reveals two noticeable differences. First, the plot shows considerably more structure in the region of space where the density is appreciable. This is understandable, as one is looking at the potential closer to the nuclear cores, and thus, greater variations in the density and potential are plausible. However, the second and striking discrepancy is that the potential difference does not seem to level off outside the region of space where the valence electron density is appreciable. On first sight, this looks like a serious problem since the extended BJ potential was derived by enforcing that v_{xc} should fall off to zero. This condition seems to be violated here. In the following, we explain this observation, showing that it is a natural consequence of a feature of the BJ construction which, to the best of our knowledge, had not been revealed so far.

First, consider a system without an external dipole field, that is, $F = 0$ in eq 2. In ref 32, it was argued that subtracting the term $\sqrt{-2\varepsilon_{\max}}$ ensures that $v_x^{\text{BJ}}(\mathbf{r})$ falls off to zero as $r \rightarrow \infty$. This argument assumed that the density is dominated by the highest occupied orbital as $r \rightarrow \infty$. This condition

appears to be a very natural one and is fulfilled almost everywhere in space—but not necessarily on nodal surfaces of the highest-occupied Kohn–Sham orbital. Therefore, the extended BJ expression can go to a nonvanishing asymptotic constant on nodal surfaces of the highest-occupied Kohn–Sham orbital that extend to infinity. We have checked this explicitly for the example of the Carbon atom and indeed find that the extended BJ expression goes to a nonvanishing constant on the nodal line. Although this feature may appear spurious on first sight, it is in fact a good one because it is shared by the exact Kohn–Sham exchange potential. The latter is also known to exhibit nonvanishing asymptotic constants on nodal surfaces of the highest occupied orbital.^{41,42}

The surprising asymptotics seen for the potential difference at $x = 0.2$ au in Figure 3 have a similar origin. In ref 32, the term $-Fz/\sqrt{-2\varepsilon_{\max}}$, compare eq 2, was introduced to enforce the condition that v_x falls off to 0 asymptotically also for a system in an external dipole field. The derivation was based on the argument that asymptotically, the density is dominated by the highest occupied orbital. However, the polyacetylene segments which we study here have a highest occupied orbital for which the molecular plane is a nodal surface. Thus, similar to the no-field case discussed in the previous paragraph, the field-counteracting term involving the highest occupied eigenvalue will enforce the proper boundary condition $v_{xc}(\mathbf{r} \rightarrow \infty) \rightarrow 0$ everywhere except for points lying on nodal surfaces of the highest occupied orbital extending to infinity. When one is not exactly on but quite close to a nodal surface, v_{xc} will fall off to 0 eventually. However, the closer one is to the nodal surface, the farther away from the molecule one has to go in order to see this falloff. In practical calculations, this region can be so far out that it is not on the numerical grid. This is the explanation for the surprising behavior of the $x = 0.2$ au curve in the left half of Figure 3.

Finally, we address a technical question. Our real-space grid technique requires us to use pseudopotentials to

eliminate the nuclear singularity. Therefore, one may ask how far this influences the results for the polarizability. For the hydrogen atom, the pseudopotential does not model core electrons but simply “smoothes” the nuclear divergence. Thus, the pseudopotential approximation is particularly harmless for H, and we have found that it makes practically no difference for the polarizability calculation whether one uses a norm-conserving pseudopotential⁴³ or a local one.⁴⁴ But even for carbon, the influence of the pseudopotential on the polarizability is small. Switching from a standard LDA norm-conserving pseudopotential⁴³ to a self-consistently constructed exact-exchange pseudopotential⁴⁵ has a small but visible influence on the plots in Figure 3 due to the changed eigenvalues, but changes in the polarizability are less than 1%, that is, on a scale that is irrelevant for the purposes of our work.⁴⁶

3. The Becke–Johnson Expression and the Exchange Virial Relation

Having seen that the extended BJ approach may offer a chance to solve the static charge-transfer problem on the basis of only semilocal functional ingredients, it is a natural next step to investigate how the BJ approach can be turned into a generally usable density functional. To this end, one needs to find an energy functional corresponding to the extended BJ potential.

One possible way of defining an energy functional corresponding to a given exchange potential ν_x is to employ the Levy–Perdew exchange virial relation³³

$$E_x = - \int n(\mathbf{r}) \mathbf{r} \cdot \nabla \nu_x(\mathbf{r}) d^3r \quad (3)$$

In the case that $\nu_x(\mathbf{r})$ is a functional derivative, the virial relation will yield the correct value of the energy functional of which $\nu_x(\mathbf{r})$ is the functional derivative. The problem is, however, that eq 3 will also yield some energy value if $\nu_x(\mathbf{r})$ is not a functional derivative. Whether that value has physical meaning is not clear.

In the context of polarizability calculations, a simple test of $E_x - \nu_x$ correspondence is given by comparing the polarizability one obtains from the first derivative of the dipole moment (as described above) to the one obtained from the second derivative of the energy with respect to the applied field. The former is the value which directly reflects the potential and is thus the right one to look at when investigating potential approximations. The latter reflects the energy expression. When the employed potential is the one that minimizes the employed energy expression, the two values one obtains for α should match. In this case, discrepancies are only an indication for possible limitations of the numerical quality of the calculation. However, if the rigorous connection between energy functional and potential is severed, this inconsistency manifests in noticeable differences between the results obtained by the two ways of calculating the polarizability. This has previously been discussed and tested³⁶ for the KLI approximation³ to the exchange-only OEP. There, the polarizabilities obtained from μ and E differed noticeably, although the KLI exchange ground-state energy is typically very close to the OEP exchange energy.

Table 2. Differences in Percentage between the Longitudinal Polarizabilities for Polyacetylene Units as Obtained by Taking the Second Derivative with Respect to the Field of the Energy and the First Derivative of the Dipole Moment^a

	C ₄ H ₆	C ₆ H ₈	C ₈ H ₁₀	C ₁₀ H ₁₂	C ₁₂ H ₁₄	C ₁₄ H ₁₆
LDA	<1	<1	<1	<1	1	2
ext. BJ	42	51	56	64	85	101

^a cf. Table 1. For the extended BJ functional, the virial energy of eq 3 was used.

Performing this test for whether using the virial expression directly can be a reasonable way of defining an energy functional corresponding to the BJ potential, we have calculated the polarizabilities also from the energy. With respect to polarizabilities obtained from the dipole moment reported in Table 1, we find pronounced differences. They are reported in Table 2. The comparison with LDA, also given in Table 2, shows that this is not a problem of numerical accuracy. This finding is in line with calculations that reported considerable discrepancies for virial energies.⁴⁹ Following the above logic, we have to conclude that the extended BJ potential is not a functional derivative. This seems highly plausible in view of the conjecture that the Slater potential is not a functional derivative⁴⁷ and that quite generally it is a nontrivial requirement that a given function be a functional derivative.⁴⁸ Therefore, simply using the virial expression with the BJ potential is not a rigorous way of defining a consistent energy-potential pair.

One might adopt an alternative point of view and look at the BJ potential in a way similar to the one adopted for the KLI and other⁸ approximate potential expressions. In this way of thinking, the proper energy expression is the Fock exchange energy, and the BJ potential is an approximation to the exchange-only OEP. However, trying to “discuss away” the problem of energy-potential consistency in this manner in our opinion is not a long-term solution either. Ultimately, the extended BJ approach should show its true strengths and capabilities in time-dependent DFT, because a time-dependent extension of the BJ approach (or some other semilocal construction sharing its main features) may solve the problem of long-range charge-transfer excitations in a computationally easy way. But without being a proper functional derivative, the potential most likely will suffer from the same problems that were observed for, for example, the time-dependent KLI potential.⁵⁰

One possible way of obtaining a consistent $E_x - \nu_x$ pair having the important features of the BJ expression is to use eq 3 in a different way. One may take the point of view that plugging the BJ expression into the right-hand side of eq 3 defines an energy functional. The potential corresponding to this energy expression must then be obtained by taking the functional derivative of this energy with respect to the density. One may hope that, in this way, one can derive a potential that is “as close as possible” to the BJ potential, but at the same time being a functional derivative. Having tried this approach in practice does not make it look very promising, though. Considering just one part of the BJ potential for simplicity, for example, the Slater potential for a system with N occupied orbitals

$$\nu_x^{\text{Slater}}(\mathbf{r}) = -\frac{1}{n} \int \frac{|\sum_{i=1}^N \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d^3 r' \quad (4)$$

plugging this into the right-hand side of eq 3 and taking the functional derivative $\delta/\delta n$ after some lengthy algebra leads to the potential

$$\begin{aligned} \nu_x^{\text{intSlater}}(\mathbf{r}) = & \frac{2}{n(\mathbf{r})} \int \frac{\sum_{i=1}^N \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \times \\ & [\sum_{i=1}^N \varphi_i^*(\mathbf{r}') (\mathbf{r} \cdot \nabla) \varphi_i(\mathbf{r})] d^3 r' - \\ & \frac{1}{n(\mathbf{r})} \int \frac{(\sum_{i=1}^N \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}'))^2}{|\mathbf{r} - \mathbf{r}'|} [\mathbf{r}(\mathbf{r} - \mathbf{r}')] d^3 r' - \\ & \frac{1}{n(\mathbf{r})} \left[3 + 2 \frac{(\mathbf{r} \cdot \nabla) n(\mathbf{r})}{n(\mathbf{r})} \right] \nu_x^{\text{Slater}}(\mathbf{r}) + \\ & \int d^3 r' \int d^3 r'' \int d^3 r''' [3n(\mathbf{r}') + (\mathbf{r}' \cdot \nabla') n(\mathbf{r}')] \times \\ & \frac{1}{n(\mathbf{r}')} \sum_{i=1}^N 2\chi_{\text{KS}}^{-1}(\mathbf{r}, \mathbf{r}''') \frac{\sum_{k=1}^N \varphi_k^*(\mathbf{r}') \varphi_k(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|} \times \\ & \left[\frac{\delta \varphi_i(\mathbf{r}')}{\delta \nu_{\text{KS}}(\mathbf{r}'')} \varphi_i(\mathbf{r}'') + \frac{\delta \varphi_i(\mathbf{r}'')}{\delta \nu_{\text{KS}}(\mathbf{r}''')} \varphi_i(\mathbf{r}''') \right] \quad (5) \end{aligned}$$

with $\nu_{\text{KS}}(\mathbf{r})$ denoting the Kohn–Sham potential and χ_{KS}^{-1} the inverse of the Kohn–Sham response function. This is not a pleasant equation. Similarly, having to take the functional derivative of ν_x^{corr} with respect to the density quickly becomes involved as the functional chain rule must be invoked to calculate the functional derivatives of the Kohn–Sham orbitals. Thus, this approach, as far as we can tell, leads to expressions that are more complicated than the exact exchange OEP equation itself. The beauty of the BJ expression, which to a considerable extent lies in its simplicity, is thus lost.

From a pragmatic point of view and for certain applications, it may be possible to define an energy via one of the routes discussed above. But one has to face the fact that presently there is no rigorous or conceptually satisfying way of defining an energy corresponding to the BJ potential. On the other hand, being able to construct an easy-to-evaluate semilocal functional that will capture the essence of the charge-transfer physics is such a tempting idea that we believe it is a worthwhile task to continue working on.

In this manuscript, we demonstrated the capabilities of such “potential functionals” by showing that the extended BJ potential leads to much better polarizabilities of polyacetylene molecules than typical semilocal functionals. We further showed that there is a yet closer similarity between the BJ expression and the exact exchange potential than previously discussed, as both lead to nonvanishing asymptotic constants on nodal surfaces of the highest occupied orbital that extend to infinity. We demonstrated that, for the systems studied here, the BJ potential can be used in combination with pseudopotentials without a relevant loss of accuracy. Finally, we critically discussed ways of how a consistent energy- and potential-functional pair may be found.

Future work will focus on three aspects. First, it appears quite feasible to eliminate the Slater potential. This was

already discussed by Becke and Johnson in their original work,³¹ and this step will not only make the functional computationally yet more attractive, it will also ameliorate the problem of making the potential a functional derivative. Second, it may be possible to replace ν_x^{corr} by a different orbital expression,⁵¹ or possibly even by an expression which does not depend on the Kohn–Sham orbitals explicitly. Again, this will not only improve computational efficiency but may also allow for writing the potential in such a way that eq 3 can be used for a proper “functional integration”. Third, extending the BJ approach to the time domain⁵¹ may be a way of constructing an exchange–correlation functional that can handle dynamical long-range charge transfer. Thus, semilocal functionals may still offer greater possibilities than what one typically expects from them.

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