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Garnet K-L. Chan, David J. Tozer, and Nicholas C. Handy

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Correlation potentials and functionals in Hartree-Fock-Kohn-Sham theory

Garnet K-L. Chan, David J. Tozer, and Nicholas C. Handy

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, United Kingdom

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We compute molecular Hartree-Fock-Kohn-Sham correlation potentials from *ab initio* coupled-cluster densities via a modified Zhao, Morrison and Parr [Phys. Rev. A, **50**, (1994) 2138] scheme involving exact exchange. We examine the potential for several small systems, and observe complex structure. By fitting a functional expansion to our potentials we obtain a closed-shell functional which is an improvement over other pure correlation functionals in Hartree-Fock-Kohn-Sham calculations. The leading term in our functional is dependent on the number of electrons. Our results lead us to question the utility of correlation defined within the Hartree-Fock-Kohn-Sham scheme, and to consider alternative partitionings of the exchange-correlation energy. © 1997 American Institute of Physics. [S0021-9606(97)00429-7]

I. INTRODUCTION

In recent years Kohn-Sham density functional theory^{1,2} has become a very popular technique in quantum chemistry. The Kohn-Sham orbitals are the eigenfunctions of a one-electron operator involving the multiplicative exchange-correlation potential, which is the functional derivative of the exchange-correlation energy functional. One possible way forward in Kohn-Sham theory is to use *ab initio* electron densities to compute exchange-correlation potentials, and then go on to construct functionals through least-squares refinement to these data.³ We are actively pursuing this approach.

An alternative density functional formalism is Hartree-Fock-Kohn-Sham (HFKS) theory.^{2,4} In this method the exchange-correlation functional is partitioned as

$$E_{xc} = E_x^{\text{HF}} + E_c \quad (1)$$

where E_x^{HF} is the Hartree-Fock orbital exchange functional, which for closed-shell systems is

$$E_x^{\text{HF}} = - \sum_{i,j} \int \int \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_1) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2) \phi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (2)$$

and E_c is the HFKS correlation functional. The resulting one-electron equations involve the regular non-multiplicative exchange operator, together with the HFKS correlation potential

$$v_c(\mathbf{r}) = \frac{\delta E_c[\rho]}{\delta \rho(\mathbf{r})}. \quad (3)$$

The aim of this paper is to compute and present molecular HFKS correlation potentials, and use this data in a least-squares procedure to construct new HFKS correlation functionals.

Several workers have computed correlation potentials through an alternative partitioning involving the optimized effective potential (OEP).^{5,6} In particular we refer to the work of Smith, Jagannathan and Handler,⁷ Pedroza,⁸ Aryasetiawan and Stott,⁹ Sahni, Gruenebaum and Perdew,¹⁰

Almbladh and Pedroza,¹¹ Davidson,¹² Umrigar and Gonze,¹³ and Chen *et al.*¹⁴ These studies have focused largely on two-electron systems where the two partitionings are equivalent, and where the potential can be obtained from a simple numerical inversion of the Kohn-Sham equations. For larger molecular systems, however, we must consider a new method for computing HFKS potentials. One possible approach is to modify existing techniques for computing exchange-correlation potentials. Gritsenko *et al.*¹⁵ have described a modification of their scheme, although their correlation potentials are not those of HFKS theory. In sections II and III we describe a modification of the Zhao, Morrison, Parr procedure,¹⁶ involving the addition of the Hartree-Fock orbital exchange functional, where the resulting potentials are those of HFKS theory, to within an additive constant. In section IV we examine the behavior of our computed correlation potentials, and in section V we report our attempts to least-squares fit a functional expansion derivative to the potentials. Our conclusions are presented in section VI.

II. THE COMPUTATION OF $v_c(\mathbf{r})$

We have previously used the Zhao, Morrison, and Parr¹⁶ (ZMP) method for calculating exchange-correlation potentials, and we now describe a variant (hereafter termed ZMPX) for computation of closed-shell HFKS correlation potentials. In HFKS theory, the total electronic energy functional is

$$E[\rho] = E^{\text{HF}}[\rho] + E_c[\rho] \\ = T_s[\rho] + E_{\text{ext}}[\rho] + J[\rho] + E_x^{\text{HF}}[\rho] + E_c[\rho]. \quad (4)$$

By analogy with the constrained search of Levy and Perdew^{4,17} we define the orbital dependent functionals T_s and E_x of HFKS theory by

$$\begin{aligned}
 T_s + E_x &= \min_{\Psi_D \rightarrow \rho_0} \langle \Psi_D | T + X | \Psi_D \rangle \\
 &= \min_{2 \sum_i \phi_i^2 \rightarrow \rho_0} \left[\sum_i -\langle \phi_i | \nabla^2 | \phi_i \rangle \right. \\
 &\quad \left. - \sum_{i,j} \int \int \frac{\phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_1) \phi_i(\mathbf{r}_2) \phi_j(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \right].
 \end{aligned} \tag{5}$$

Following ZMP we enforce the constrained minimization in Eq. (5) through a Lagrange multiplier λ associated with the self-repulsion quantity

$$\begin{aligned}
 C &= \frac{1}{2} \int \int \frac{[\rho^\lambda(\mathbf{r}_1) - \rho_0(\mathbf{r}_1)][\rho^\lambda(\mathbf{r}_2) - \rho_0(\mathbf{r}_2)]}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \\
 &= 0,
 \end{aligned} \tag{6}$$

and we introduce the usual Lagrange multipliers ϵ_i for diagonal orthonormality constraints. Explicit functionals of the density are added to bring the Lagrangian into the usual HFKS form, and minimization with respect to orbital variations gives the one-electron equations

$$\begin{aligned}
 &\left(-\frac{1}{2} \nabla_1^2 + v_{\text{ext}}^\lambda(\mathbf{r}_1) + v_J^\lambda(\mathbf{r}_1) + v_X^\lambda(\mathbf{r}_1) + v_C^\lambda(\mathbf{r}_1) - \epsilon_i \right) \\
 &\quad \times \phi_i^\lambda(\mathbf{r}_1) = 0,
 \end{aligned} \tag{7}$$

where

$$\begin{aligned}
 v_J^\lambda(\mathbf{r}_1) &= \int \frac{\rho^\lambda(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2, \\
 v_C^\lambda(\mathbf{r}_1) &= \lambda \int \frac{[\rho^\lambda(\mathbf{r}_2) - \rho_0(\mathbf{r}_2)]}{r_{12}} d\mathbf{r}_2, \\
 v_X^\lambda(\mathbf{r}_1) &= - \sum_j \int d\mathbf{r}_2 \frac{\phi_j^\lambda(\mathbf{r}_2) \phi_j^\lambda(\mathbf{r}_1)}{r_{12}} P_{12},
 \end{aligned} \tag{8}$$

and

$$\rho^\lambda = 2 \sum_i |\phi_i^\lambda|^2. \tag{9}$$

Given that $\rho^\lambda(\mathbf{r}) = \rho_0(\mathbf{r})$ at the solution point, the Lagrange multiplier λ must be infinite. Identifying Eq. (7) as the HFKS equations therefore gives the HFKS correlation potential as $\lim_{\lambda \rightarrow \infty} v_C^\lambda(\mathbf{r})$ to within an additive constant (since the ZMPX potential vanishes asymptotically by construction). Also observe that the exact exchange gives a self-interaction free correlation potential and so there is no reason to add the Fermi-Amaldi factor $(1 - 1/N)$ ¹⁸ used in the regular ZMP method. We have incorporated the above procedure in our original ZMP code^{19,20} which uses a quadratically convergent SCF scheme as described by Bacskay.²¹

III. Finite-basis, finite-lambda ZMPX methods

The ZMPX method yields the correlation potential that gives the input density $\rho_0(\mathbf{r})$, and so is limited by the accu-

racy of the *ab initio* density used. In our studies we use Brueckner Doubles (BD) relaxed densities generated using CADPAC²² with Gaussian TZ2P basis sets. These basis sets are Dunning contractions²³ of Huzinaga primitive sets.²⁴ For B, C, N, O, F and Ne, it is a 10s6p to 5s4p contraction with two sets of polarization functions with exponents 1.05 and 0.35, 1.2 and 0.4, 1.35 and 0.45, 1.35 and 0.45, 2.0 and 0.67, and 2.4 and 0.6 respectively. For Li and H the contractions are 10s to 4s and 5s to 3s respectively and the two sets of polarization functions have exponents 0.4 and 0.1 and 1.5 and 0.5 respectively.

It is possible that the input BD density may not be non-interacting v -representable, in which case taking the limit $\lambda \rightarrow \infty$ will give incorrect results. However the success of the various schemes to compute exchange-correlation potentials indicates that this problem, for the equilibrium ground-states of molecules, remains a formal one.

A problem of much greater importance is the finite basis used to solve the ZMPX equations. There will always be a residual error in the density because the correlated density is not exactly representable by a single Kohn-Sham determinant in a finite basis. Consequently, taking the limit $\lambda \rightarrow \infty$ will result in a potential and eigenvalues that diverge with increasing λ . In our previous investigations of the ZMP equations we determined an optimum value of the Lagrange multiplier $\lambda_{\text{opt}}^{\text{ZMP}}$ by expanding the residual quantity $\int |\rho^\lambda(\mathbf{r}) - \rho_0(\mathbf{r})| d\mathbf{r}$ for large λ ²⁰, but such expansions do not work well in the ZMPX scheme. However the similar λ dependence of $\epsilon_{\text{homo}}^{\text{ZMP}}$ and $\epsilon_{\text{homo}}^{\text{ZMPX}}$ suggests that we may still use $\lambda_{\text{opt}}^{\text{ZMP}}$ in our calculations. We were encouraged by the agreement between our correlation potential for He (determined with $\lambda_{\text{opt}}^{\text{ZMP}}$) and that of Umrigar and Gonze,¹³ obtained from an accurate numerical inversion of the Kohn-Sham equations. For the set of ten molecules studied in this paper, we use $\lambda = 900$.²⁰

IV. FEATURES OF $v_C(\mathbf{r})$ AND ϵ_{homo}

In Figures 1(a)-1(d) we present plots of the correlation potential for Ne, N₂, F₂, and CO. The correlation potentials are approximately an order of magnitude smaller than the corresponding exchange-correlation potentials presented in Ref. 20. We expect the general features to be correct, but the small magnitude of the correlation potentials suggests that the quality of the basis sets, the input density, and particularly the choice of λ will limit the accuracy. We observe rich structure in the potential which oscillates between negative and positive values, which is in agreement with previous observations.⁷⁻¹⁴ For Ne, the early turning points coincide with those of the radial density distribution. The oscillatory nature suggests that any successful fit to $v_C(\mathbf{r})$ will require high-order gradient terms, such as the Laplacian of the density $\nabla^2 \rho$.

Despite the complicated behavior of $v_C(\mathbf{r})$ there are certain general features we can understand. Hartree-Fock theory is well-known to produce shell structure in the radial density distribution of atoms. It is instructive to see how this arises in the He atom in the RHF theory for which

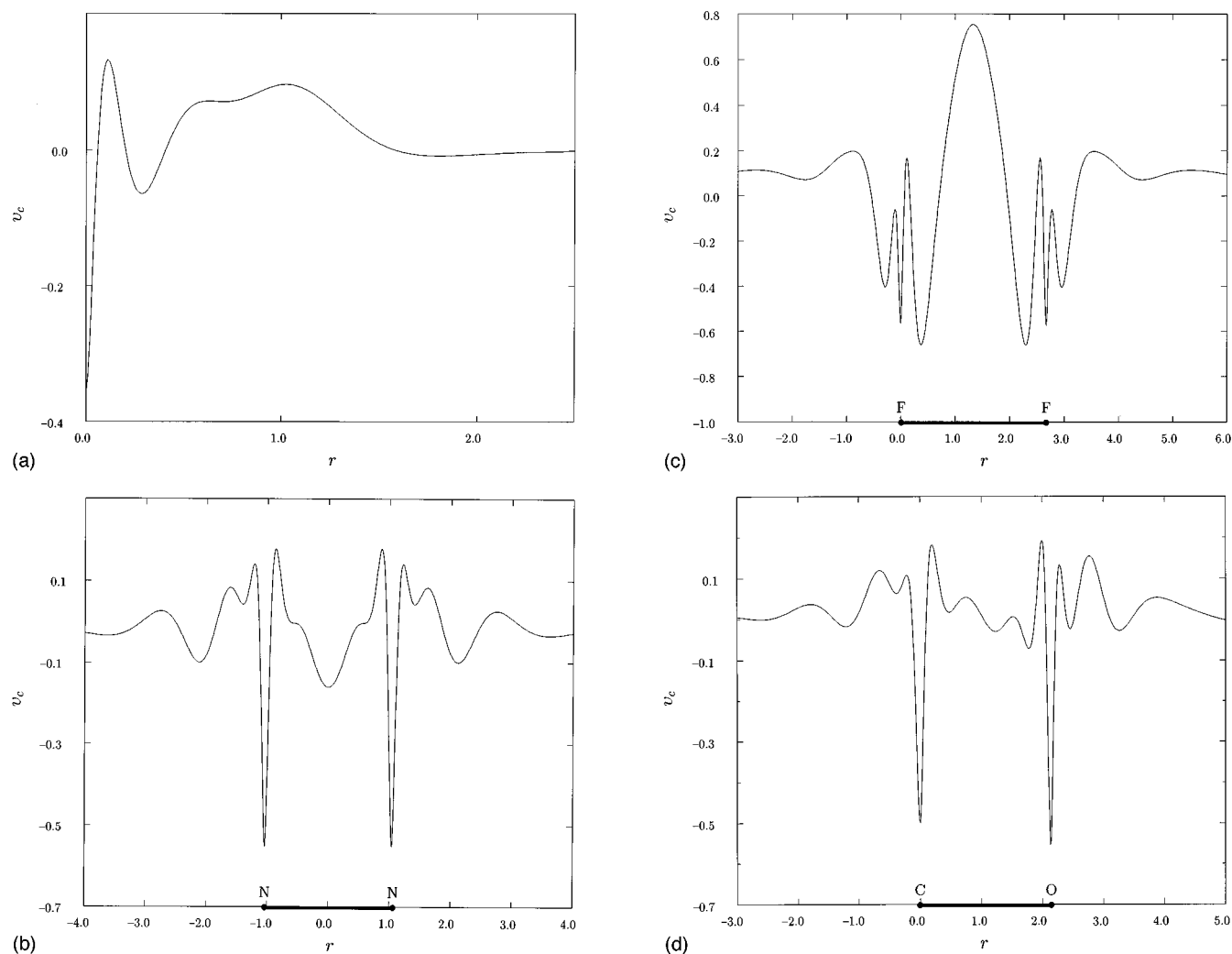


FIG. 1. The ZMPX correlation potential (in a.u.) for (a) Ne, (b) N_2 , (c) F_2 , and (d) CO. For Ne the potential is plotted against r . For the diatomics it is plotted along the bond axis, for zero radial distance.

$$-\frac{1}{2}\nabla^2\phi(\mathbf{r}_1)=\left(\epsilon-\int\frac{\rho(\mathbf{r}_2)}{r_{12}}d\mathbf{r}_2+\frac{2}{\mathbf{r}_1}\right)\phi(\mathbf{r}_1). \quad (10)$$

If we solve this equation iteratively and substitute $\exp(-\alpha\mathbf{r}_1)$ as a first guess,²⁵ we obtain an additional turning point in ∇^2 (indicative of shell structure²⁶) from the turning point in the Coulomb potential. However a more flexible unrestricted and correlated wavefunction will give a density with additional shell fine structure. The analogous HFKS theory must reproduce the additional shell fine structure associated with the correlation and this is one reason for the highly oscillatory correlation potential.

A universal observation in the systems studied is a negative $v_c(\mathbf{r})$ near the nucleus, which contracts the HF density near the nucleus. This is consistent with previous studies of correlation potentials in neutral systems.^{7–14} Particularly interesting is the fact that $v_c(\mathbf{r})$ at the nuclei is related to the atomic electronegativity. This can be clearly seen when comparing the plots for the isoelectronic molecules, CO and N_2 . If we examine the N_2 plot we also observe large oscillations between the atoms and unlike in the exchange–correlation

potential,²⁰ at the bond midpoint there is a minimum rather than a maximum. The frequency of the oscillations decreases away from the nuclei. We observe that the magnitude of the correlation potential is relatively large everywhere in the F_2 molecule, which may be related to the poor Hartree–Fock description of this system.

We now consider the behavior in the core and asymptotic regions. Accurate studies of the correlation potential¹³ have shown that it is approximately quadratic near the nucleus. We observe the correct quadratic behavior, although our input densities are poor near the nucleus since we use Gaussian basis sets which cannot reproduce the cusp in the density. Chen *et al.*¹⁴ have recently proposed that at large r , $v_c(\mathbf{r})$ approaches its asymptotic limit from above if $I < -\epsilon_{\text{homo}}^{\text{HF}}$, and that the converse is also true. This rule they interpret in terms of first-order perturbation theory where

$$I \sim -(\epsilon_{\text{homo}}^{\text{HF}} + \langle \phi_{\text{homo}} | v_c | \phi_{\text{homo}} \rangle). \quad (11)$$

We have examined the correlation potential far away ($15 a_0$) from the origin in our ten systems. Although we might ex-

pect from the above rule that the potential should generally be positive far away we do not observe this behavior. However our potentials far away exhibit slow oscillatory behavior which is probably an artifact due to the inaccuracy of the input density at long range. Thus we cannot draw definite conclusions concerning the above rule.

In figures 2(a) and 2(b) we compare the ZMPX correlation potential for Ne with the potentials of the local VWN²⁷ and gradient-corrected PW91C^{28–30} functionals. These potentials completely fail to reproduce the complex features of $v_c(\mathbf{r})$. This is in keeping with previous observations³¹ that existing correlation functionals, despite giving good total energies, give poor potentials and thus poor densities and ionization energies. How can a potential with such poor behavior give a good energy? We suggest that total energies do not give strong bounds on the behavior of $v_c(\mathbf{r})$. A plausible justification is provided by the upper bound for the Kohn–Sham correlation energy³²

$$E_c \leq - \int \rho(\mathbf{r}) \mathbf{r} \cdot \nabla v_c(\mathbf{r}) d\mathbf{r}. \quad (12)$$

Although the KS correlation energy defined in Ref. 32 is not the same as the HFKS correlation energy defined by the partitioning of Eq. (1), they are numerically very similar,¹⁴ and thus we might expect the same bound to hold for the HFKS correlation energy as well. We observe from figures 2(a) and 2(b) that the VWN and PW91C potentials are generally negative (the Jacobian effectively eliminates the positive divergence in PW91C) and increase smoothly with $|\mathbf{r}|$ and thus will give negative correlation energies despite having such poor behavior.

Finally we observe that the HOMO energy determined by our scheme, $\epsilon_{\text{homo}}^{\text{ZMPX}}$, is generally closer to $-I$ than $\epsilon_{\text{homo}}^{\text{HF}}$ (see the values in Table II). We expect this behavior of a correlation potential which vanishes at infinity and which is approximately parallel to the exact correlation potential.³³ This confirms the accuracy of our procedure and our input density. In the cases where the Hartree–Fock eigenvalue is closer, we attribute this to fortuitous cancellation of correlation and relaxation effects.

V. FUNCTIONAL EXPANSIONS

In this section we describe our attempts to construct HFKS correlation energy functionals by least-squares refinement to ZMPX correlation potentials. We choose a functional form for E_c containing variable parameters, and compute its functional derivative $v_c^{\text{fit}}(\mathbf{r})$. The parameters are then optimized by minimizing a generalized version of the quantity in Ref. 3

$$\Omega = \sum_{\text{molecules}} \int [v_c^{\text{fit}}(\mathbf{r}) - v_c^{\text{ZMPX}}(\mathbf{r})]^2 \rho^a(\mathbf{r}) d\mathbf{r}. \quad (13)$$

We note that if we include infinite flexibility in our functional and carry out the minimization above over all densities, we will recover an exchange–correlation functional which differs from the exact exchange–correlation functional only by terms which functionally differentiate to zero. Here

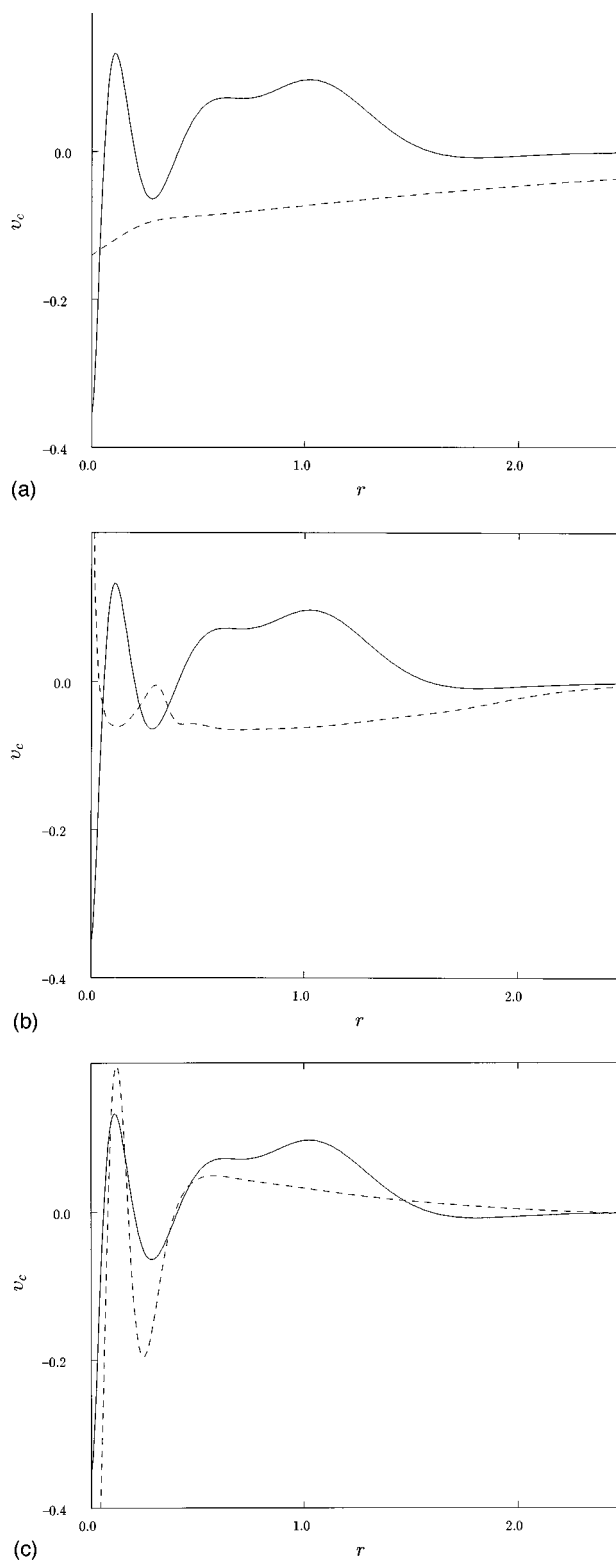


FIG. 2. The ZMPX correlation potential (in a.u.) for Ne (solid curve), plotted as a function of r . This is compared with the potential (dashed curves) of (a) VWN, (b) PW91C, and (c) F_{lin}^{12} .

we use BD densities and density gradients, and ZMPX correlation potentials (which are approximately parallel to the true correlation potentials, but may differ by an additive constant) and carry out the minimization over a training set of

data for H₂, H₂O, HF, CO, F₂, BH, LiH, CH₄, N₂, and Ne. We have examined several local and gradient-corrected functional forms such as the expansion

$$F_{\text{lin}} = \int \sum_i c_i \rho^{n_i} x^{m_i} d\mathbf{r} \quad (14)$$

with

$$x = \frac{|\nabla \rho|}{\rho^{4/3}}, \quad (15)$$

where n_i were restricted to multiples of 1/6 and x to integers as in Ref. 3, and the resulting equations are linear least-squares. We have also examined more flexible forms requiring non-linear fitting procedures, where we allow n_i and m_i to be optimized, and we term these functionals $F_{\text{nl}}^{\text{lin}}$. Finally, we have examined Padé approximant forms such as a Wigner-like functional

$$F_{\text{Padé1}} = \int \frac{c_1 \rho^{n_1}}{1 + c_2 \rho^{n_2}} d\mathbf{r} \quad (16)$$

and a gradient-corrected form

$$F_{\text{Padé2}} = \int \frac{c_1 \rho^{n_1} + c_2 \rho^{n_2} x^{m_2}}{1 + c_3 \rho^{n_3} + c_4 \rho^{n_4} x^{m_4}} d\mathbf{r}. \quad (17)$$

In our previous attempts to fit functional expansions to ZMP exchange–correlation potentials we have found that a positive term, proportional to the number of electrons, must be added to the energy functional to obtain accurate energetics.³ This term introduces a constant into the potential, which consequently does not vanish asymptotically, and is consistent with the need to average over the discontinuity in the exchange–correlation potential as the electron number crosses integer. In Kohn–Sham theory it can be shown^{34,35} that for an open-shell system where $\epsilon_{\text{homo}} = \epsilon_{\text{lumo}}$, the asymptotic potential is $(I - A)/2$ where I and A are the ionization potential and electron affinity respectively. In HFKS theory, matters are complicated by the presence of exact exchange. However from the above, we should not be surprised if we have to add analogous terms in our fits to HFKS correlation potentials. We note that Liu and Parr³⁶ also explicitly introduce a term proportional to the number of electrons when they fit correlation functionals to total energies, and many other researchers have also pointed out the need for explicitly N -dependent functionals.^{12,37}

A. Fitting to the correlation potential

We have investigated how well the above forms can represent the correlation potential. Increasing the value of the parameter a in Eq. (13) reduces the percentage error, and we feel that a value of 2/3 is near-optimal. Comparing $F_{\text{nl}}^{\text{lin}}$ with F_{lin} we find little improvement in optimizing the powers as well as the linear coefficients, and the optimization becomes sensitive to the starting guess. It is more desirable to add more terms to F_{lin} , which follows from the fact that the correlation potential is not easily fitted to a short truncated expansion in powers of ρ and x . Unfortunately, increasing the number of parameters can introduce numerical instabili-

TABLE I. Optimized parameters n_i , m_i , and c_i (see Eq. (14)) for the F_{lin}^{12} correlation functional.

n_i	m_i	c_i
7/6	0	-0.051484
8/6	0	+0.105250
9/6	0	+0.006794
10/6	0	-0.014952
10/6	1	+0.031501
11/6	1	-0.085141
12/6	1	+0.051996
13/6	1	-0.009132
14/6	2	+0.003251
15/6	2	-0.003836
16/6	2	+0.001495
17/6	2	-0.000193

ties and successive coefficients alternate in sign. The results using the Padé forms were disappointing. Substantially more work is needed to optimize Padé forms as the non-linear fits are sensitive to the starting position. In this work we will therefore concentrate on a 12 parameter linear expansion denoted F_{lin}^{12} whose optimized parameters are presented in Table I.

The Ω value for this functional is 0.669 which compares with a reference value

$$\Omega_{\text{ref}} = \int \rho^a(\mathbf{r}) [v_c^{\text{ZMPX}}(\mathbf{r})]^2 d\mathbf{r}. \quad (18)$$

of 0.844, giving a percentage error ($100\% \times \Omega / \Omega_{\text{ref}}$) of almost 80%. However, in figure 2(c) we compare the Ne potential associated with F_{lin}^{12} with the ZMPX potential, and there is reasonable qualitative agreement. The large percentage error in the fit is not simply a result of the oscillatory nature of the potential – we can fit very well to any single system (with errors of only 10%). Instead it demonstrates that $v_c(\mathbf{r})$ is a highly non-local potential and it is this non-locality which produces the wide variety of oscillations in the different systems.

The failure of all of the above forms to fit the correlation potential highlights the complex nature of the correlation in conventional post-Hartree-Fock techniques. Certainly if we include higher derivatives and more terms in the functional expansion then we can expect a better fit. However we must question whether it is sensible to fit to the correlation potential as defined by the partitioning of Eq. (1). We have obtained significantly smaller percentage errors when fitting to the exchange–correlation potential as a whole,³ which would suggest some cancellation of non-locality in $v_{\text{xc}}(\mathbf{r})$. Indeed, this is consistent with the recent observation that subtracting the Fermi–Amaldi potential (which in some respects represents exchange in regular ZMP theory) from the ZMP exchange–correlation potential results in a potential which is more non-local than $v_{\text{xc}}(\mathbf{r})$ itself.²⁰

Our results highlight the fact that if we are to partition the exchange–correlation energy and fit to the residual correlation potential, we must optimize the partitioning to minimize the non-locality. In the light of these comments we

TABLE II. Negative of the highest occupied eigenvalue (in a.u.) for F_{lin}^{12} , compared to VWN_x, PW91C_x, BLYP, H-F, and the ZMPX values. I is the experimental ionization energy, and Δ is the mean absolute error.

	VWN _x	PW91C _x	F_{lin}^{12}	ZMPX	BLYP	H-F	I
H ₂	0.652	0.628	0.628	0.585	0.377	0.596	0.567
LiH	0.341	0.325	0.294	0.307	0.157	0.297	0.283
BH	0.392	0.376	0.343	0.328	0.200	0.347	0.359
CH ₄	0.601	0.583	0.535	0.530	0.343	0.547	0.460
N ₂	0.682	0.672	0.613	0.624	0.373	0.626	0.573
CO	0.603	0.570	0.544	0.537	0.329	0.552	0.515
HF	0.706	0.689	0.636	0.622	0.342	0.649	0.590
F ₂	0.705	0.682	0.640	0.629	0.347	0.649	0.577
Ne	0.909	0.890	0.834	0.817	0.484	0.849	0.792
H ₂ O	0.562	0.531	0.497	0.487	0.254	0.508	0.463
Δ	0.097	0.077	0.043	0.035	0.197	0.047	

suggest that the hybrid functionals introduced by Becke,³⁸ which include only a fraction of the true exchange, may offer the flexibility to find some optimized partitioning.

B. Performance of the fitted functional

In this section we examine the performance of the F_{lin}^{12} functional defined in Table I. Despite the poor overall fit, we might expect this functional to give a better potential than existing functionals in some “average” way. The functional derivative of F_{lin}^{12} vanishes at infinity although, being a functional of ρ and $|\nabla\rho|$ alone, it must diverge at cusps in the density.¹³ In Tables II–VI we examine self-consistent eigenvalues, geometries, and total energies for molecules both present and absent from the training set. We compare our HFKS F_{lin}^{12} results with those from HFKS calculations using the VWN and PW91C functionals. We denote these methods VWN_x and PW91C_x where the subscript denotes exact exchange. We also present Hartree-Fock (H-F) and Kohn-Sham BLYP results. All calculations were performed using large quadrature grids and TZ2P quality basis sets as described previously.

In Table II we present self-consistent highest occupied eigenvalues, at optimized geometries, computed using F_{lin}^{12} , VWN_x, PW91C_x, BLYP, and H-F. We also present the non-self-consistent values from the ZMPX procedure. The F_{lin}^{12}

TABLE III. Negative of the highest occupied eigenvalue (in a.u.) for F_{lin}^{12} , compared to VWN_x, PW91C_x, BLYP, and H-F. I is the experimental ionization energy, and Δ is the mean absolute error.

	VWN _x	PW91C _x	F_{lin}^{12}	BLYP	H-F	I
CO ₂	0.601	0.588	0.534	0.329	0.546	0.506
C ₂ H ₂	0.466	0.456	0.407	0.257	0.416	0.419
C ₂ H ₄	0.430	0.422	0.372	0.241	0.380	0.386
NH ₃	0.475	0.461	0.410	0.217	0.425	0.373
H ₂ O ₂	0.530	0.511	0.470	0.234	0.479	0.387
O ₃	0.550	0.537	0.479	0.288	0.494	0.457
Li ₂	0.212	0.203	0.183	0.113	0.180	0.188
HCN	0.548	0.548	0.494	0.325	0.505	0.500
Δ	0.075	0.064	0.027	0.148	0.030	

TABLE IV. Optimized geometries (Å and degrees) for molecules in the training set computed using the fitted functional F_{lin}^{12} , VWN_x, PW91C_x, BLYP and H-F compared with the experimental results. Δ is the mean absolute error in the bond lengths.

		VWN _x	PW91C _x	F_{lin}^{12}	BLYP	H-F	Expt
H ₂	r(HH)	0.719	0.729	0.741	0.744	0.732	0.741
H ₂ O	r(OH)	0.929	0.931	0.949	0.971	0.940	0.957
	θ (HOH)	106.6	106.4	106.3	106.4	106.3	104.5
N ₂	r(NN)	1.058	1.059	1.073	1.104	1.067	1.098
HF	r(HF)	0.888	0.889	0.905	0.933	0.898	0.917
F ₂	r(FF)	1.319	1.305	1.351	1.440	1.335	1.412
BH	r(BH)	1.198	1.213	1.234	1.240	1.220	1.232
LiH	r(LiH)	1.565	1.577	1.617	1.598	1.598	1.596
CO	r(CO)	1.094	1.095	1.110	1.137	1.103	1.128
CH ₄	r(CH)	1.066	1.071	1.093	1.094	1.082	1.086
Δ		0.036	0.032	0.016	0.010	0.022	

values are very close to the ZMPX values, demonstrating that our fit accurately describes the asymptotic regions of the ZMPX potential. The F_{lin}^{12} values are closer to $-I$ than any other method, including Hartree-Fock. In Table III we present values for molecules that are absent from the training set, and draw similar conclusions.

Next consider the optimized geometries in Tables IV and V. The addition of the VWN and PW91C correlation functionals to the Hartree-Fock functional results in a significant shortening of the bond lengths. Hartree-Fock theory is known to underestimate bond lengths,^{31,39} and so the accuracy of these post-Hartree-Fock methods is poorer still. This can be traced to the introduction of dynamic correlation, and is consistent with our view that fitting to energies alone does not always yield accurate functionals. In contrast, the effect

TABLE V. Optimized geometries (Å and degrees) for molecules absent from the training set computed using the fitted functional F_{lin}^{12} , VWN_x, PW91C_x, BLYP and H-F compared with the experimental results. Δ is the mean absolute error in the bond lengths, and Δ_2 is the mean absolute error in the bond lengths excluding Li₂.

		VWN _x	PW91C _x	F_{lin}^{12}	BLYP	H-F	Expt
C ₂ H ₂	r(CC)	1.167	1.170	1.188	1.205	1.180	1.203
	r(CH)	1.041	1.048	1.063	1.067	1.054	1.063
C ₂ H ₄	r(CC)	1.299	1.300	1.326	1.335	1.314	1.331
	r(CH)	1.059	1.065	1.084	1.088	1.074	1.081
	θ (HCH)	116.8	117.0	116.7	116.5	116.8	117.1
CO ₂	r(CO)	1.125	1.125	1.143	1.174	1.136	1.160
O ₃	r(OO)	1.183	1.176	1.210	1.293	1.196	1.272
	θ (OOO)	119.2	119.2	119.1	118.0	119.2	116.8
H ₂ O ₂	r(OH)	0.931	0.934	0.950	0.977	0.942	0.963
	r(OO)	1.370	1.355	1.411	1.496	1.390	1.450
	θ (OOH)	103.2	103.3	102.6	99.3	102.9	99.4
Li ₂	r(LiLi)	2.704	2.739	2.813	2.724	2.785	2.673
NH ₃	r(NH)	0.985	0.989	1.008	1.021	0.998	1.012
	θ (HNH)	108.1	107.8	107.7	106.4	107.7	106.7
HCN	r(CH)	1.051	1.051	1.066	1.072	1.057	1.065
	r(CN)	1.116	1.116	1.131	1.158	1.124	1.153
Δ		0.038	0.041	0.027	0.015	0.033	
Δ_2		0.044	0.039	0.016	0.012	0.026	

TABLE VI. Absolute errors in total energies (in E_h) computed using F_{lin}^{12} , $F2_{\text{lin}}^{12}$, VWN_x, PW91C_x, BLYP, and H-F at the optimized geometries. Δ is the mean absolute error.

	VWN _x	PW91C _x	F_{lin}^{12}	BLYP	H-F	$\Delta E_{F_{\text{lin}}^{12}}/N$	$F2_{\text{lin}}^{12}$
H ₂	0.056	0.007	0.040	0.004	0.042	0.020	0.038
LiH	0.133	0.007	0.107	0.002	0.087	0.027	0.048
BH	0.192	0.001	0.172	0.007	0.159	0.029	0.061
CH ₄	0.296	0.023	0.358	0.011	0.299	0.036	0.031
N ₂	0.392	0.063	0.638	0.017	0.556	0.046	0.094
CO	0.410	0.109	0.622	0.023	0.542	0.044	0.077
HF	0.311	0.026	0.467	0.023	0.349	0.047	0.078
F ₂	0.541	0.086	0.888	0.071	0.764	0.049	0.187
Ne	0.344	0.020	0.464	0.019	0.403	0.046	0.074
H ₂ O	0.290	0.085	0.450	0.011	0.376	0.045	0.061
Δ	0.297	0.043	0.421	0.019	0.362		0.075

^aThe exact energies for the 10 systems (Ref. 41) are -1.173 , -8.070 , -25.289 , -40.513 , -109.543 , -113.325 , -100.458 , -199.529 , -128.939 , and $-76.437 E_h$, respectively.

of our F_{lin}^{12} correlation functional is generally to lengthen the bonds, resulting in an improvement over Hartree-Fock theory. This is again a result of our better representation of the correlation potential, which determines the nuclear derivative of the HFKS correlation energy.

For molecules outside the training set the mean absolute error ($\Delta = 0.027 \text{ \AA}$) with F_{lin}^{12} rises considerably, as does that of H-F ($\Delta = 0.033 \text{ \AA}$). The main contribution to the absolute error is from the bond length of Li₂ which is overestimated by 0.14 \AA with F_{lin}^{12} . Disregarding this result, our mean absolute error with F_{lin}^{12} ($\Delta = 0.016 \text{ \AA}$) is again a significant improvement over H-F ($\Delta = 0.026 \text{ \AA}$). We believe that the poor performance of F_{lin}^{12} , and indeed all the other correlation functionals, for Li₂ arises from the poor performance of Hartree-Fock theory for this system.

In Table VI we present the errors in the total energies for various density functionals. The energies of the F_{lin}^{12} functional are significantly above the exact values, and following Ref. 3 we examine these errors as a function of the number of electrons. The ratio of the energy error to the number of electrons is more variable than was observed for exchange-correlation fits, which is what we expect since the correlation energy in one-electron systems is zero. However it is clear that the addition of a term proportional to the number of electrons will still improve the energies significantly. In Table VI we also present results for

$$F2_{\text{lin}}^{12} = F_{\text{lin}}^{12} - 0.0389 \int \rho(\mathbf{r}) d\mathbf{r}, \quad (19)$$

where we have chosen the constant by averaging the absolute error in the energy per electron over all the molecules. However, the value is very different to the $+0.186$ obtained by fitting to exchange-correlation potentials.³ This follows because the exact exchange contribution to the HFKS equations is naturally discontinuous, and picks up the majority of the required discontinuity. Although molecules generally belong to the intermediate density regime, apart from very near

the nuclei, the limiting behavior of this ratio for large N may still be related to the exact high density results⁴⁰

$$E_c = \int \rho \epsilon_c d\mathbf{r}, \quad (20)$$

$$\epsilon_c = 0.0311 \ln r_s - 0.048 + r_s (A^0 \ln r_s + C^0), \quad (21)$$

$$\frac{4}{3} \pi r_s^3 = \frac{1}{\rho}. \quad (22)$$

As N increases for our systems, our constant does appear to approach -0.048 . Finally we observe that we do not expect a large energy contribution from a highly oscillatory potential, and we observe that this N -dependent term in fact dominates the contribution to the correlation energy. Indeed our value of -0.0389 is very close to that of Liu and Parr³⁶ who obtained $c = -0.0377$ by fitting cN to atomic energies.

VI. CONCLUSIONS

We have computed HFKS correlation potentials from a modified Zhao, Morrison, Parr¹⁶ scheme involving exact exchange. The computed potentials have a highly non-local structure and are chemically interesting as they reflect the nature of the atoms in the molecules. We have attempted to fit the derivatives of functional expansions to these potentials, although we experienced great difficulties due to the non-local behavior. These observations strongly suggest that starting from the HFKS approach to density functional theory is not desirable, despite the small magnitude of the correlation energy defined within the HFKS partitioning. It is well known that VWN_x and PW91C_x perform poorly, and this can be understood in the light of our results. Our best functional is an improvement over these functionals and Hartree-Fock theory, although it is by no means satisfactory. In line with recent research in this area, we find that a term dependent on the number of electrons does improve the total energies. The constant in the potential arising from this term differs significantly from the constant obtained when we fit to exchange-correlation potentials.³ Exact exchange clearly has an important influence, and we are continuing to investigate it.

If we are to include exact exchange in density functional theory, then our results emphasize the importance of partitioning the exchange-correlation energy in such a way that the residual is maximally local. A detailed study of this locality is required. We suggest that the flexibility of hybrid functionals may allow us to find such an optimum partitioning.

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