

Accurate numerical determination of Kohn-Sham potentials from electronic densities: I. Two-electron systems

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(Received 3 January 1997; accepted 12 March 1997)

The extraction of the true Kohn-Sham exchange-correlation potential from near-exact electronic densities is demonstrated, with particular reference to the two-electron systems He and H₂. It is shown that if the reference density is obtained from a standard configuration interaction calculation, very large orbital basis sets are required to obtain convergence in the resulting exchange-correlation potential. The correlation contribution to molecular bonding is analysed in terms of contributions from the potential in different regions of real space. © 1997 American Institute of Physics. [S0021-9606(97)01323-8]

I. INTRODUCTION

Interest in applying density-functional theory (DFT) to molecular electronic structure continues to grow. However, there is still much room for improvement in the form of the energy functional before DFT can be applied routinely with confidence of high accuracy. Within the Kohn-Sham (KS) formalism,¹ it is the exchange-correlation energy $E_{xc}[\rho]$ and its associated functional derivative $v_{xc}[\rho]$ which is the critical quantity. Commonly used approximations include the uniform electron gas derived local density approximations (LDA) (Refs. 2 and 3) and various functionals involving the gradient of the density.^{4–6}

One route towards the design of improved functionals is through the analysis of the form of exact or near-exact electronic densities for trial systems. It is a consequence of the first Hohenberg-Kohn theorem that within the KS formalism, there is a unique exchange-correlation potential which can be viewed as being determined by the density. Although v_{xc} does not give E_{xc} directly, the information obtained is nonetheless useful. For example, potential energy surfaces can be obtained within an additive constant by integration,⁷ and knowledge of the exact v_{xc} is helpful in the search for improved approximate density functionals. A number of authors have explored this idea, producing v_{xc} from accurate *ab initio* densities for a number of systems.^{8–19} It is one of the purposes of this paper to investigate the accuracy with which this procedure can be performed. We will show that unless very accurate densities, and very flexible representations of the KS orbitals and v_{xc} are used, significant errors can arise. We present accurate results for two-electron systems, with *N*-electron molecules to follow in a later paper.

The techniques used to obtain v_{xc} may be considered as broadly divided into two classes, “direct” and “iterative”. The direct approach is applicable to two-electron singlet systems where the single Kohn-Sham orbital ϕ is represented as the square root of half the density ρ , and so the single Kohn-Sham equation (following Smith, Jagannathan and Handler⁸) is given by

$$(-\frac{1}{2}\nabla^2 + v_N + v_J + v_{xc})\rho^{1/2} = \epsilon\rho^{1/2}. \quad (1)$$

Here, if the external potential, v_N , the Coulomb potential, v_J , and the effect of the kinetic energy operator upon the Kohn-Sham orbital may be calculated, then the exchange-correlation potential, v_{xc} , will be known to within a constant shift.

The “iterative” approaches have been developed to obtain v_{xc} from densities where obtaining the underlying Kohn-Sham orbitals is not a problem with a unique solution, as it is for the “direct” approach. The method generally employed is to start with a set of orbitals within a self-consistent procedure which produce an *N*-representable electronic density, and minimise the difference between this self-consistent (SC) density and the “exact” (or reference) density ρ_0 , subject to the constraint²⁰ that the self-consistent KS orbitals are those which minimise the kinetic energy for a given electronic density. This constraint can be expressed symbolically, following Zhao and Parr,¹² as

$$\min_{\Phi_D \rightarrow \rho_0} \left\langle \Phi_D \left| -\frac{1}{2} \sum_i^N \nabla_i^2 \right| \Phi_D \right\rangle, \quad (2)$$

where Φ_D is the determinantal wavefunction or orbital product. Zhao, Parr and co-workers^{12,14} have developed an approach which introduces a constraint potential dependent upon the difference between the SC and reference densities. Others, principally Gritsenko, van Leeuwen and Baerends,¹⁷ have also used iterative procedures which depend upon convergence of the SC density to the reference density also seek to produce the exchange-correlation potential.^{15,18}

We have found that there are difficulties in using basis set and grid techniques together for obtaining the exchange-correlation potential; these arise from the incompleteness of the basis set and can allow a set of different potentials given on the grid to represent the same density. This is clearly a problem in the light of the first Hohenberg-Kohn theorem²¹ which states that there is a unique mapping between the ground state density and the external potential to within an

additive constant. The problem manifests itself in two ways. During a self-consistent Kohn-Sham procedure (as in Hartree-Fock) the occupied-virtual block of the Molecular orbital representation of the Kohn-Sham Matrix contains zero elements at convergence. If we represent a potential v as a linear combination of functions of a complete basis set, i.e.,

$$v = \sum_i^{\infty} c_i \chi_i, \quad (3)$$

then a matrix element coupling an occupied molecular orbital ϕ_{μ} and a virtual one ϕ_{σ} through this potential is given by

$$V_{\mu\sigma} = \int \phi_{\mu}^* v \phi_{\sigma} d\tau. \quad (4)$$

Where an incomplete set is used to describe the orbital basis, there will be a set of non-zero linear combinations of the basis describing the potential which will lie outside the incomplete orbital basis, and thus a number of different potentials exist which fulfill the Kohn-Sham condition for convergence within the SC procedure. This problem is not removed by representing the potential as values on a grid rather than as a linear combination of functions.

The second problem arising from an incompleteness in the orbital basis set is the difficulty of representing the exact density from a multi-reference calculation sufficiently accurately with a single determinant built from Kohn-Sham orbitals represented in the same basis set. This may make it impossible for the iterative methods to converge to a SC density which is equal to the reference density. Indeed, workers have reported unexplained difficulties in this convergence which might be explained by incompleteness.¹⁴

Given that these problems exist, we suggest alleviating them using a fully numerical approach where all functions are described on a numerical grid. In the next section we outline aspects of the numerical procedure. In this paper we present results for the two electron system which have been obtained numerically, which corresponds to using a "direct" method, as described above.

II. NUMERICAL EVALUATION OF THE KOHN-SHAM POTENTIAL

For a two-electron system within a restricted Kohn-Sham procedure, we may rearrange equation (1) to represent the exchange-correlation potential as

$$v_{xc} = \epsilon + \frac{1}{2} \rho^{-1/2} \nabla^2 \rho^{1/2} - v_N - v_J. \quad (5)$$

We term this "inversion;" if we know the external potential v_N and the Coulomb potential v_J then the term second term on the right-hand side, namely the local kinetic energy which involves the Laplacian, is the one presenting the greatest challenge to calculate, followed by the Coulomb potential, v_J .

If the density has been determined from a density matrix represented in a spectral basis, we can choose to determine

the local kinetic energy and the Coulomb potential either numerically or analytically; where the density is not so represented then we must either fit the density to a basis or tackle the problem numerically. For a density from a single orbital system the local kinetic energy can be expressed as

$$-\frac{1}{2} \rho^{-1/2} \nabla^2 \rho^{1/2} = \frac{1}{8} \rho^{-2} \nabla \rho \cdot \nabla \rho - \frac{1}{4} \rho^{-1} \nabla^2 \rho. \quad (6)$$

If the density is given by the function $\rho(r) = \exp(-2ar)$, then from equation (6) the local kinetic energy is given by

$$-\frac{1}{2} \exp(ar) \nabla^2 \exp(-ar) = \frac{a}{r} - \frac{a^2}{2}. \quad (7)$$

If, instead, the density is given by a Gaussian function, $\rho(r) = \exp(-2ar^2)$ then the local kinetic energy is given by

$$-\frac{1}{2} \exp(ar^2) \nabla^2 \exp(-ar^2) = 3a - 2a^2 r^2. \quad (8)$$

If the density is given analytically in a basis (or product basis) and the analytic derivatives are available then the determination of the local kinetic energy through equation (6) is straightforward. The density, however, is not always available analytically so that if the local kinetic energy is required we must obtain this numerically, for instance, by using the recently developed sparse interpolative operator approach.²²

The long range behaviour of the local kinetic energy term should allow it to asymptotically go to a constant finite value, and so the appearance of $\rho^{-1/2}$ should not cause difficulties for an exponentially decaying density. It should be noted, however, that for a gaussian representation of the density, the local kinetic energy in the long range diverges parabolically [see equation (8)], dependent upon the exponent of the most diffuse function; this has important consequences for the design of density functionals involving the Laplacian and higher derivatives of the density when Gaussian basis sets are employed.²³

We have validated the accuracy of the numerical radial laplacian operator by comparing the local kinetic energy of a Hartree-Fock derived orbital calculated numerically with that calculated analytically for a set spherical densities from one and two electron systems. The results for an exponentially decaying radial function are shown in figure 1. The analytic result is given in equation (7). Figure 1 shows the absolute value of the difference between the numerical result obtained on a 100 point Log3 grid²⁴ with the scale factor $\alpha = 10$ a.u. This shows the numerical evaluation of the local kinetic energy across the range of r from 10^{-4} bohr to 5.0 bohr differs from the analytic result by less than 1.5×10^{-6} a.u.

The Coulomb potential, v_J , may be calculated by a number of methods, both analytically and numerically;²² a number of these are discussed by Termath and Handy²⁵ and the sparse interpolative operator approach can be used to solve Poisson's equation to obtain the potential directly from the density.²²

There is the matter of the shift, ϵ , in equation (5). We determine this by subtracting energy of the 1-electron from the from the CI energy of the 2-electron system, giving us the ionisation potential. While this will not be exact it will allow us to present results which only differ by a small shift.

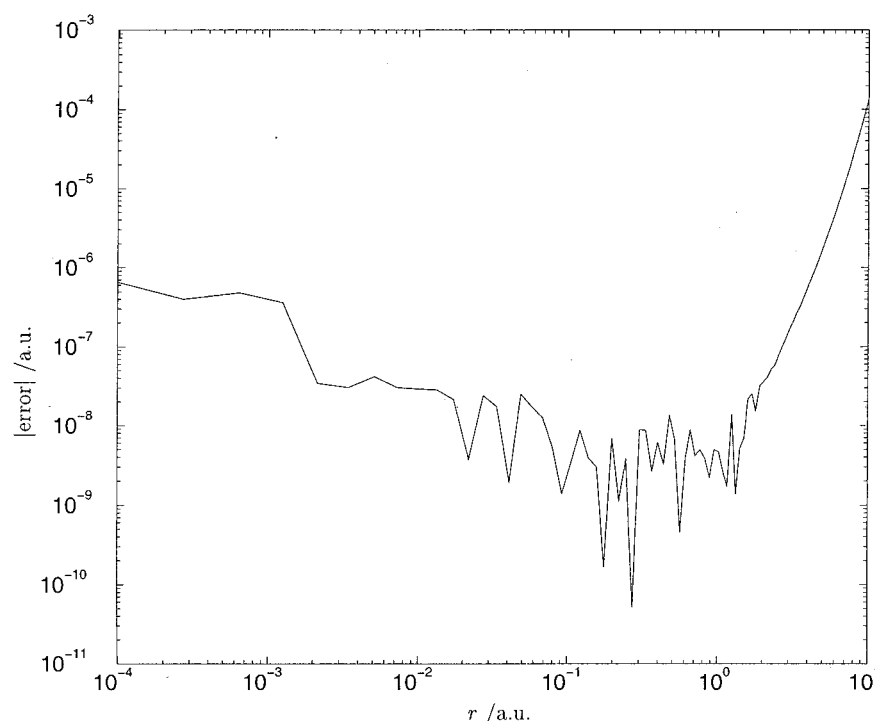


FIG. 1. The plot shows the absolute value of the difference between the analytically and numerically calculated local kinetic energy $-(1/2f(r))\nabla^2 f(r)$ for $f(r) = \exp(-r)$. All quantities are in atomic units.

Atomic two-electron systems with spherical symmetry are relatively easily studied using simply a radial grid and a radial representation of the Laplacian. They do represent, however, extremely important benchmark systems for calibrating other methods. In the next section we present the results for the helium spin singlet ground state.

III. HELIUM GROUND STATE SINGLET

We first present results for a set of CI densities calculated for the closed shell singlet ground state of helium, using a variety of different Gaussian basis sets. For the single spatial orbital we know that the Hartree-Fock exchange potential is related to the Hartree-Fock Coulomb potential by

$$v_x = -\frac{1}{2}v_J^{\text{HF}}, \quad (9)$$

so this provides a very useful guide to the accuracy of the calculated potential. For the CI-calculated Coulomb potential we define the self-interaction energy to be

$$v_{\text{self}} = \frac{1}{2}v_J, \quad (10)$$

and this allows a partial separation of exchange and correlation effects through the definition of the correlation potential as

$$v_c = v_{\text{xc}} - \frac{1}{2}v_J. \quad (11)$$

What size of Gaussian basis set should be used to obtain credible results? To answer this a set of different common basis sets were used to produce densities which, in turn, were used to produce the exchange-correlation potential by “in-

version.” The basis sets used were STO-3G,²⁶ and the correlation-consistent sequence cc-pVDZ,²⁷ cc-pVTZ,²⁷ cc-pVQZ,²⁷ cc-pV5Z²⁷ and cc-pV6Z-h (Ref. 28) (-h means that no h functions were used). The results in figure 2 show that as the quality of the basis is increased, the curvature of exchange-correlation potential is seen to reduce. The effects can be divided into near nuclear and long range effects. Both arise from the inability of the basis to adequately represent the local kinetic energy. In the near nuclear region, as noted by Smith *et al.*,⁸ the variationally calculated energy is not highly dependent upon an accurate representation of the near nuclear wavefunction. This, coupled with the poor representation of the cusp by the Gaussian basis functions, results in an oscillation in the local kinetic energy and, thus, the exchange-correlation potential. This is remedied by improving the basis set through the introduction of additional s functions with large exponents. The long range behaviour is dominated by the Gaussian functions with a small exponent through equation (8). The introduction of diffuse functions will help reduce this problem in the intermediate range but will not ultimately remove this problem.

To improve the short and long range density, increasingly larger even-tempered s Gaussian basis sets²⁹ and diffuse s sets were used to replace the s functions in the cc-pVQZ basis set. In figure 3 the number of s functions of the even tempered set is given by a couple, the first number indicating the number of non-diffuse even-tempered s functions and the second indicating the number of addition diffuse s functions. Compared to figure 2, the magnitude of oscillations is greatly reduced, in particular near the nucleus.

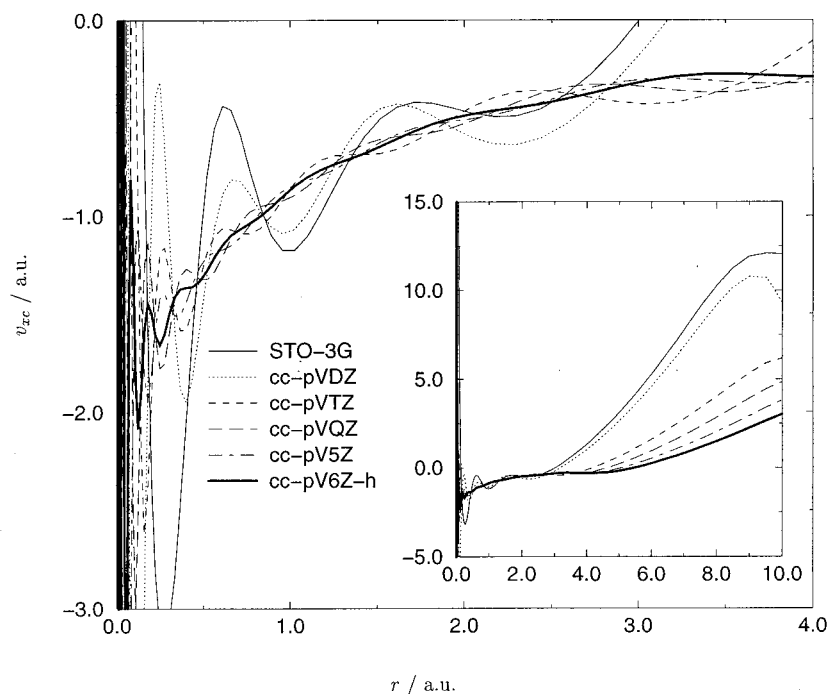


FIG. 2. The plots show the exchange correlation potential, $v_{xc}(r)$, calculated by “inversion” for the helium spin-singlet ground state using a sequence of common basis sets of increasing size. All the basis sets are uncontracted. The h functions of the cc-V6Z basis are not included. The long range behaviour of the potential is shown in the inset plot. All quantities are in atomic units.

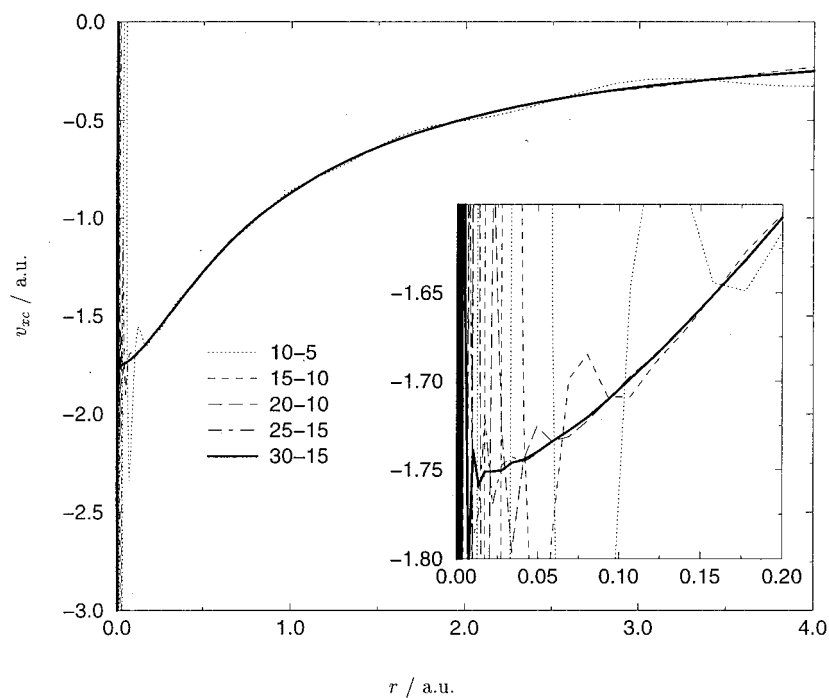


FIG. 3. The plots show the exchange correlation potential, $v_{xc}(r)$, calculated by “inversion” for the helium spin-singlet ground state using a variety of basis sets with large s orbitals. The basis sets used are the uncontracted cc-VQZ set (Ref. 27) for p, d, f functions, for the s functions an uncontracted even tempered set of functions, of size n , according to the “regular” prescription described by Schmidt and Ruedenberg (Ref. 29), Table III, and an additional m of even tempered diffuse s functions, extended using the ratio of the smallest exponents from the non-diffuse s functions. The particular basis is denoted by $n-m$. The short range behaviour is magnified in the inset plot. All quantities are in atomic units.

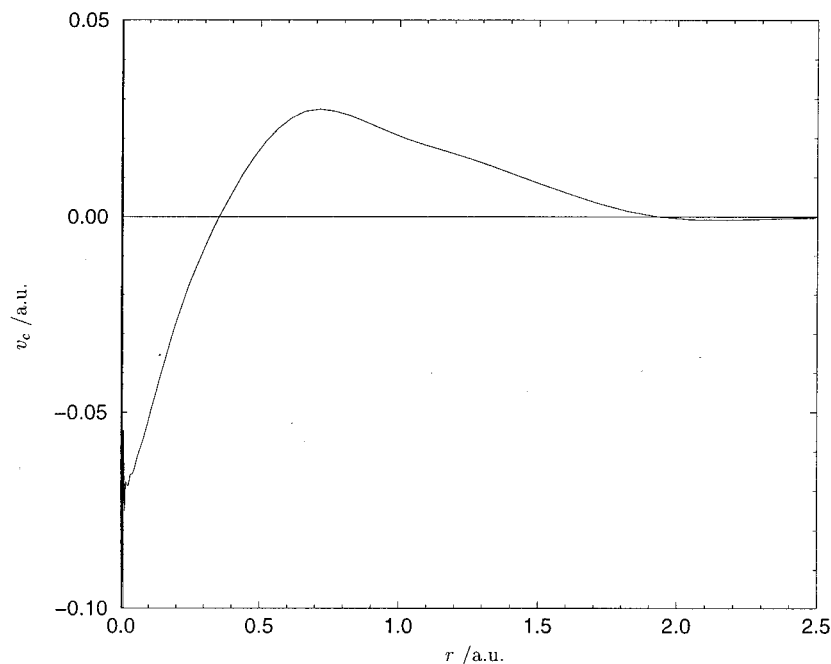


FIG. 4. The plots show the correlation potential, $v_c(r)$, calculated by “inversion” for the helium spin-singlet ground state using the 30-15 basis set. There is a small shift present in the data.

The curve for the largest basis now resembles the Hartree-Fock exchange potential, v_x . For helium, the difference between the self-interaction potential and the Hartree-Fock exchange potential is small. Figure 4 shows the correlation potential, v_c [equation (11)], using the largest of the even tempered basis set, 30–15; there is still a small shift arising from the inaccuracy in the calculation of ϵ , and some spurious oscillatory behaviour remains very close to the nucleus. This curve shows good qualitative agreement with those presented earlier in the literature.^{8,13} Small differences arise in the near nuclear region, but overall reasonable agreement is found. But if the devil is in the detail then it is very important to attempt to remove the spurious oscillations and curvature arising from the incomplete basis set before accepting the results of the “inversion” calculation. While these should be less for a Slater or hydrogenic basis set they will still be present to some extent while the basis is incomplete.

Umrigar and Gonze¹³ have provided a very detailed analysis of the correlation potential in helium-like ions, including the important observation that v_c obtained from commonly-used approximate functionals differs markedly from the exact potential; there is thus no need for us to repeat such arguments here. However, in what follows, we extend the consideration beyond atoms, and consider the nature of the correlation potential in a molecule.

IV. HYDROGEN MOLECULE GROUND STATE SINGLET

The cylindrically symmetric spin singlet ground state of the hydrogen molecule can be treated in the same manner as the spherically symmetric helium spin singlet. We obtain analytically, for a particular wavefunction expressed in a ba-

sis, the gradient and Laplacian of the density. This facilitates the calculation of the local kinetic energy through equation (6) and allows us to calculate the exchange correlation potential by “inversion” as before.

The equilibrium bond length, $R=R_e$, is taken to be 1.4 bohr. As before, the accuracy of the density is extremely important. We have employed two different basis sets, labelled A and B respectively. Basis set A is comprised of a set of even tempered s functions (30–10) and the $\{p,d,f\}$ functions coming from the cc-pVQZ prescription,³⁰ where all functions were uncontracted. Basis set B is larger, using an s set (35–10) and the $\{p,d,f,g\}$ from the cc-pV5Z prescription,³⁰ again all uncontracted. These are large basis sets; close to 99% of the correlation energy, with respect to the calculation of Kołos and Wolniewicz,³¹ is recovered by both basis sets. The residual correlation energy unaccounted for by basis A is 1.2% and by basis B is 0.65%.

Figure 5 show the correlation potential, $v_c = v_{xc} - v_{\text{self}}$, calculated with the basis sets A and B at the equilibrium bond length, R_e , and twice the equilibrium bond length. For a given bond length it is clear that despite the quality of the basis sets, the correlation potential calculated differs sufficiently to give qualitatively different results. These basis sets are better than those used for the helium calculation and yet the variation in the potential takes place at a much greater distance and with a much larger magnitude than in the helium data (shown in figure 3). It would seem from these results that the sensitivity of the density to its incomplete description by a finite spectral basis makes it very difficult to extract a unique exchange correlation potential. In the light of this the results presented in figures 6 and 7 should not be over-interpreted; some of the features may be artifacts of

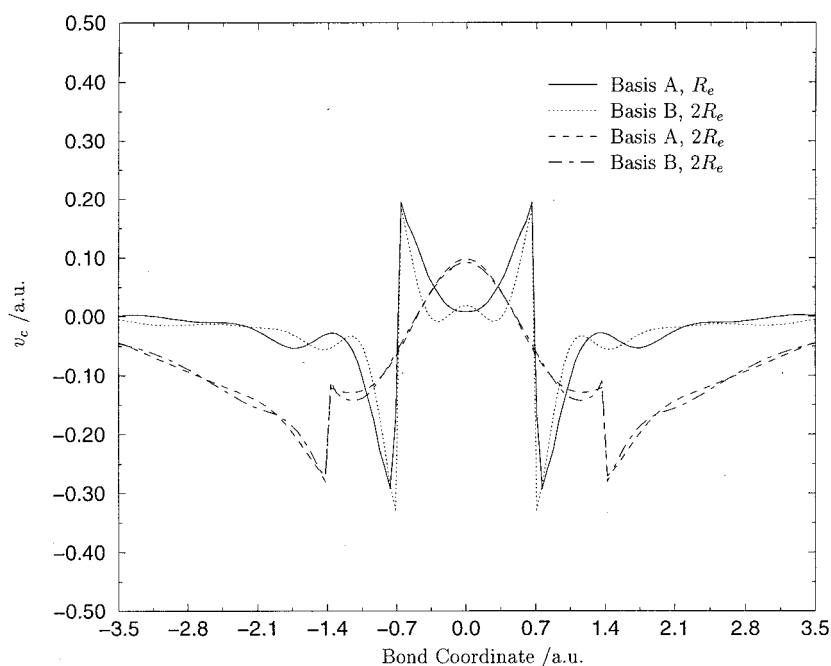


FIG. 5. The plots show the correlation potential, $v_c(r)$, calculated by “inversion” for the hydrogen molecule spin-singlet ground state using the basis sets A and B (see text) for two different bond lengths, R_e and $2R_e$.

basis set incompleteness. In equation (6) there is a balance between the term containing the gradient of the density and the term containing the Laplacian of the density. The extent to which one term dominates the other affects the local kinetic energy and, thus, the exchange correlation potential.

Figure 6 shows the correlation potential, $v_c = v_{xc} - v_{self}$, at different bond lengths along the molecular

axis, using basis set B. We note firstly that as the bond is stretched, the magnitude of the correlation potential increases; this is a reflection of the inappropriateness of v_{self} in describing exchange at large R , analogous to the failure of Hartree-Fock. At large R , v_{xc} would be a more appropriate quantity to study. However, certain general features of v_c at small and intermediate R are worthy of comment. Outside

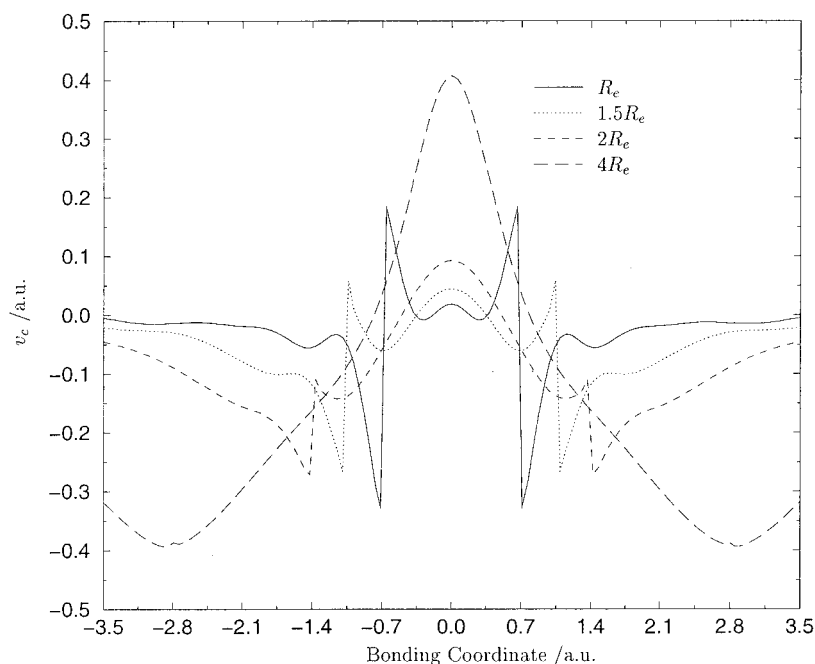


FIG. 6. The plots show the correlation potential, $v_c(r)$, calculated by “inversion” for the hydrogen molecule spin-singlet ground state using basis set B, at different internuclear bond lengths.

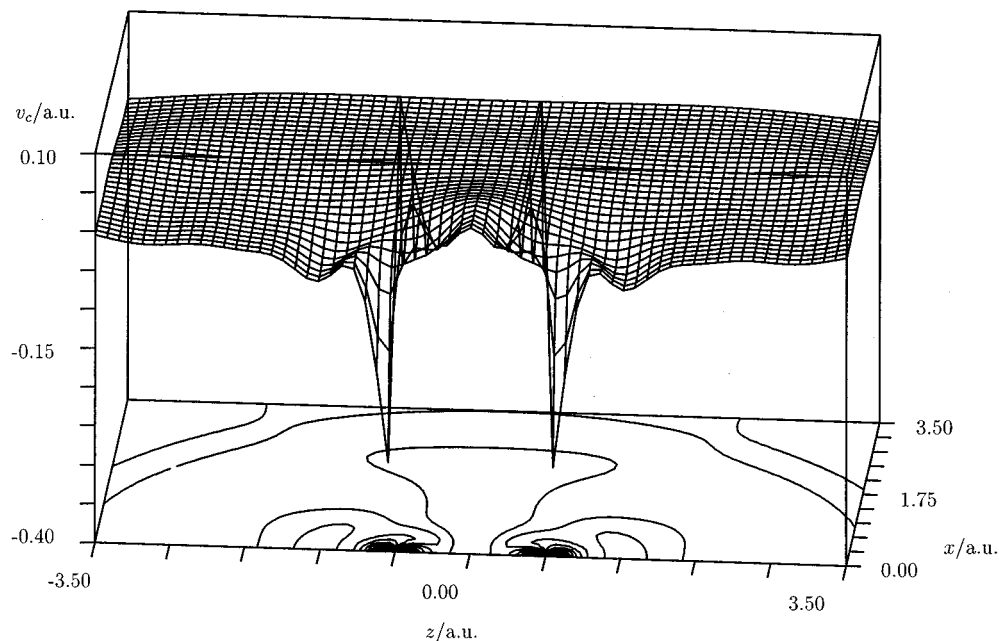


FIG. 7. The surface and contour plots show the correlation potential, $v_c(r)$, calculated by “inversion” for the hydrogen molecule spin-singlet ground state using basis set B at the internuclear bond length of $R_e = 1.4$ bohr.

the internuclear region, v_c increases from a negative value near the nucleus to zero asymptotically, just as in the atom. However, on moving through a nucleus along the bond axis, v_c changes sign abruptly. Between the nuclei it is positive near the nuclei, and near the bond centre, but dips in value in between. Figure 7 shows the off-axis behaviour of v_c at $R = R_e$. There appear to be additional topological features not seen on the axis, such as a true maximum on the plane

dividing the nuclei approximately 0.6 bohr from the bond axis. As already discussed above, however, caution is needed in such interpretation because of the possibility that the results are not fully basis-set converged.

The form of the true v_c is compared in figure 8 with the potential arising from the two standard approximate correlation potentials VWN (Ref. 3) and LYP.⁶ We note that neither of the approximate potentials bears even a remote resem-

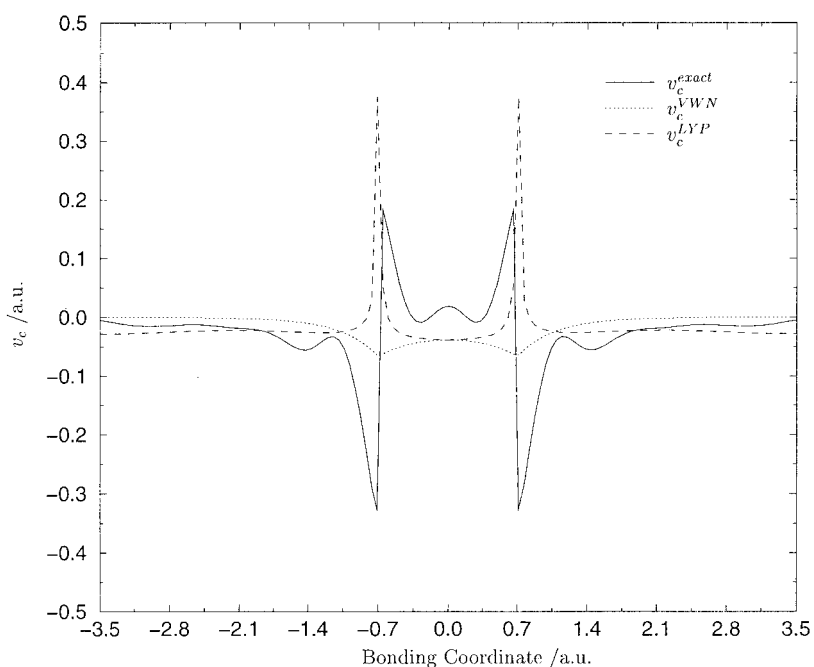


FIG. 8. The plots show the true correlation potential, $v_c(r)$, calculated by “inversion” for the hydrogen molecule spin-singlet ground state using basis set B at the internuclear bond length of $R_e = 1.4$ bohr, and the corresponding approximate correlation potentials, v_c^{VWN} and v_c^{LYP} .

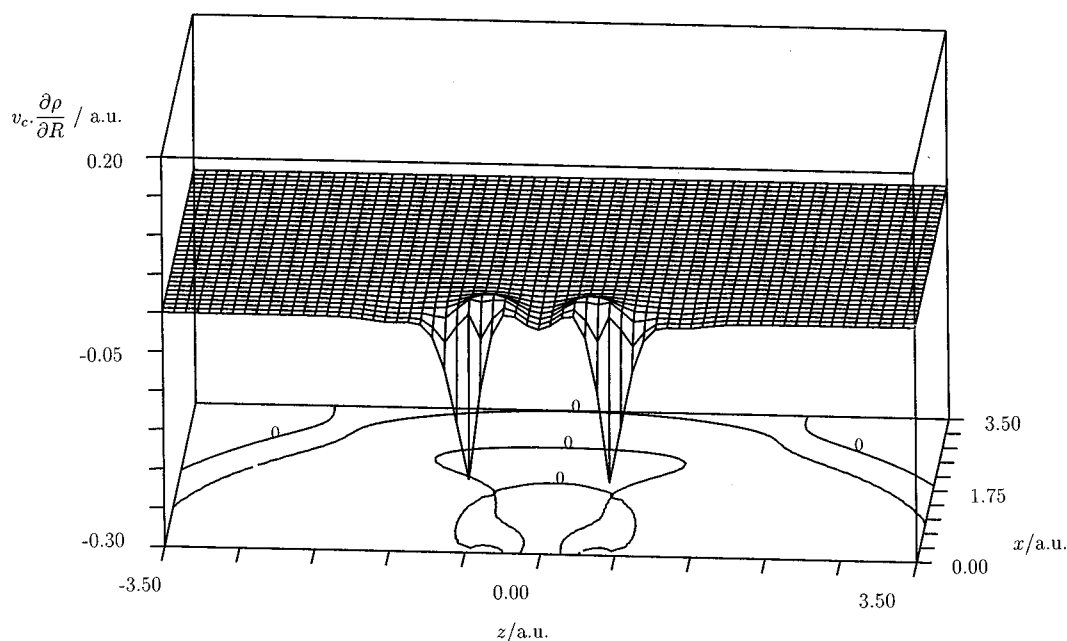


FIG. 9. The surface and contour plots show the integrand for equation 12 calculated by "inversion" for the hydrogen molecule spin-singlet ground state using basis set B at the internuclear bond length of $R_e = 1.4$ bohr.

blance to the true v_c . This difference offers a target for the design of improved density functionals.

One means of analysing the nature of v_c is through the contribution to the potential energy surface through the correlation energy E_c . Straightforward application of the calculus of variations gives^{18,7}

$$\frac{dE_c}{dR} = \int v_c \frac{\partial \rho}{\partial R} d^3\mathbf{r} \quad (12)$$

and thus v_c weighted with the gradient of the density gives directly a contribution to the force on the nuclei. Figure 9 shows the variation in \mathbf{r} space of $v_c \cdot (\partial \rho / \partial R)$ at $R = R_e$. Firstly we note that the sign change at the nucleus of v_c is exactly matched by a similar feature in $\partial \rho / \partial R$, and near the nucleus the integrand in equation (12) is uniformly negative. Although it is difficult to make an unambiguous partitioning, it seems that at least a dominant contribution to the negative integral (12) arises from the region near the nuclei, where both the potential and density derivative are large in magnitude.

V. CONCLUSIONS

We have shown that extreme care is needed in the extraction of Kohn-Sham potentials from supposed exact densities. In particular, the use of a finite basis set to represent orbitals carrying this density can lead to spurious fluctuations in the potential, and these undulations can be traced to corresponding fluctuations in the local kinetic energy. This conclusion has consequences for all attempts to use such potentials in the search for improved density functionals. We have

shown, however, that if care is taken in basis set selection, a reasonable representation of the potential can be obtained.

We have also analysed the topology of the Kohn-Sham potential in a molecule. We have shown that two of the commonly used approximate functionals have potentials which are not even remotely close to the true potential, and this will provide guidance for future research into the form of approximate density functionals. We have also explored the contribution of the correlation potential to the molecular potential energy curve.

ACKNOWLEDGMENT

This research has been supported by the EPSRC (grant GR/J83307).

- ¹W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- ²J. C. Slater, Phys. Rev. **81**, 385 (1951).
- ³S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
- ⁴J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).
- ⁵A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
- ⁶C. T. Lee, W. T. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
- ⁷M. E. Mura, P. J. Knowles, and C. A. Reynolds, Chem. Phys. Lett. **262**, 533 (1996).
- ⁸D. W. Smith, S. Jagannathan, and G. S. Handler, Int. J. Quantum Chem. Quantum Chem. Symp. **13**, 103 (1979).
- ⁹C. O. Almbladh and A. C. Pedroza, Phys. Rev. A **29**, 2322 (1984).
- ¹⁰A. C. Pedroza, Phys. Rev. A **33**, 804 (1986).
- ¹¹F. Aryasetiawan and M. J. Stott, Phys. Rev. B **38**, 2974 (1988).
- ¹²Q. S. Zhao and R. G. Parr, J. Chem. Phys. **98**, 543 (1993).
- ¹³C. J. Umrigar and X. Gonze, Phys. Rev. A **50**, 3827 (1994).
- ¹⁴Q. Zhao, R. C. Morrison, and R. G. Parr, Phys. Rev. A **50**, 2138 (1994).
- ¹⁵R. van Leeuwen and E. J. Baerends, Phys. Rev. A **49**, 2421 (1994).
- ¹⁶O. V. Gritsenko, R. van Leeuwen, and E. J. Baerends, Phys. Rev. A **52**, 1870 (1995).

- ¹⁷O. V. Gritsenko, R. van Leeuwen, and E. J. Baerends, *J. Chem. Phys.* **104**, 8535 (1996).
- ¹⁸V. E. Ingamells and N. C. Handy, *Chem. Phys. Lett.* **248**, 373 (1996).
- ¹⁹D. J. Tozer, V. E. Ingamells, and N. C. Handy, *J. Chem. Phys.* **105**, 9200 (1996).
- ²⁰M. Levy, *Proc. Natl. Acad. Sci. USA* **76**, 6062 (1979).
- ²¹P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- ²²M. E. Mura and P. J. Knowles (in preparation).
- ²³P. Jemmer and P. J. Knowles, *Phys. Rev. A* **51**, 3571 (1995).
- ²⁴M. E. Mura and P. J. Knowles, *J. Chem. Phys.* **104**, 9848 (1996).
- ²⁵V. Termath and N. C. Handy, *Chem. Phys. Lett.* **230**, 17 (1994).
- ²⁶W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.* **51**, 2657 (1969).
- ²⁷D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **100**, 2975 (1994).
- ²⁸K. A. Peterson and T. H. Dunning, Jr. (private communication).
- ²⁹M. W. Schmidt and K. Ruedenberg, *J. Chem. Phys.* **71**, 3951 (1970).
- ³⁰T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- ³¹W. Kołos and L. Wolniewicz, *J. Chem. Phys.* **49**, 404 (1968).