

Approximate kinetic-energy functionals

Daniel Joubert*, Moïse Tchoula Tchokonte

Department of Physics, University of the Witwatersrand, PO Wits, 2050 Johannesburg, South Africa

Received 1 November 1996; accepted 3 April 1997

Abstract

An approximate non-local independent fermion kinetic-energy density functional is constructed from a model for the density functional exchange hole. The functional is exact for one- and two-electron systems and gives a good approximation for a homogeneous electron gas. Reasonable results are also obtained for model systems. © 1997 Elsevier Science B.V.

Keywords: Density functional; Kinetic energy; One-electron system; Two-electron system; Electron gas

1. Introduction

In the density functional formalism [1–3] the ground state energy $E[n]$ of a system of electrons can be expressed as a functional of the ground state electron density $n(\mathbf{r})$

$$E[n] = T_s[n] + U[n] + E_{xc}[n] + \int v(\mathbf{r})n(\mathbf{r}) d^3r \quad (1)$$

where $v(\mathbf{r})$ is the external potential, $T_s[n]$ is the non-interacting kinetic energy, $U[n]$ is the classical electron–electron repulsion energy, and $E_{xc}[n]$ is the exchange–correlation energy. The exact forms of the kinetic-energy functional and the exchange–correlation functional are not known. Although the kinetic energy can be calculated in the Kohn–Sham formalism [1–3] by using an auxiliary basis, an accurate approximation to the kinetic-energy functional will enable one to compute the properties of systems of electrons by minimising Eq. (1) directly in terms of the charge density. Many approximations to the kinetic-energy

functional have appeared in the literature. These include the Thomas–Fermi local density approximation, semi-local approximations [4–8] (for a discussion of the properties of a number of semi-local approximations, see Ref. [7]) and non-local approximations [4,9]. As of yet, none of these approximations is of sufficient accuracy for calculations.

In this paper we examine a non-local approximation to the kinetic energy constructed from an approximation to the density functional exchange hole. The spherical average of the exchange hole, $n_x^{\text{av}}(\mathbf{r}, \mathbf{r} + \mathbf{s})$, is approximated by an expression of the form

$$n_x^{\text{av}}(\mathbf{r}, \mathbf{r} + \mathbf{s}) = -\frac{1}{2}n^{\text{av}}(\mathbf{r} + \mathbf{s}) \exp\{-\beta(\mathbf{r})s^2 g[n^{\text{av}}(\mathbf{r} + \mathbf{s}), \nabla_s n^{\text{av}}(\mathbf{r} + \mathbf{s})]\} \quad (2)$$

where the superscript av indicates the spherical average of an arbitrary function $f(\mathbf{r}, \mathbf{r} + \mathbf{s})$ centred at \mathbf{r}

$$f^{\text{av}}(\mathbf{r}, \mathbf{r} + \mathbf{s}) = \frac{1}{4\pi} \int d\phi_s d\theta_s \sin(\theta_s) f(\mathbf{r}, \mathbf{r} + \mathbf{s}) \quad (3)$$

The kinetic energy can be expressed in terms of the second derivative with respect to s of the spherical

* Corresponding author. E-mail: joubert@physnet.phys.wits.ac.za

average of the exchange hole, and for this approximation, Eq. (2), the kinetic energy is then given (in hartree atomic units) by

$$T_s[n] = \frac{1}{8} \int d^3r |\nabla n(\mathbf{r})|^2/n(\mathbf{r}) + \frac{3}{2} \int d^3r \beta(\mathbf{r})n(\mathbf{r})^{5/3} \quad (4)$$

where the first term in Eq. (4) is the Weizsäcker term and the second term is the Pauli term (see, for example, the discussion in Ref. [8]). It is therefore only the Pauli term that is approximated. The function $\beta(\mathbf{r})$ is determined from the sum rule

$$4\pi \int ds s^2 n^{\text{av}}(\mathbf{r}, \mathbf{r} + s) = -1 \quad (5)$$

which is an exact property of the exchange hole [2,3] and can be deduced from the definition of the exchange hole, Eq. (6). The value of $\beta(\mathbf{r})$ is dependent upon an integration over $n^{\text{av}}(\mathbf{r}, \mathbf{r} + s)$ and hence this approximation is non-local despite the apparent local form of Eq. (4).

2. Kinetic energy and the exchange hole

The density functional exchange hole is defined, in analogy to the Hartree–Fock exchange hole [2,3], as (for convenience, given here for a spin-compensated system)

$$n_x(\mathbf{r}, \mathbf{r} + s) = -\frac{1}{2} |n_1(\mathbf{r} + s)|^2/n(\mathbf{r}) \quad (6)$$

$$n_1(\mathbf{r}, \mathbf{r} + s) = \sum_i^{\text{occ}} \Psi_i(\mathbf{r})\Psi_i^*(\mathbf{r} + s) \quad (7)$$

$$n(\mathbf{r}) = \frac{1}{2} \sum_i^{\text{occ}} |\Psi_i(\mathbf{r})|^2 \quad (8)$$

where Ψ_i are the eigenfunctions of the Kohn–Sham equations [1–3]. The spherical average of $n_x(\mathbf{r}, \mathbf{r} + s)$ expanded as a series in s retains only even order terms

$$n_x^{\text{av}}(\mathbf{r}, \mathbf{r} + s) = -n(\mathbf{r})/2 + s^2 \left[\sum_i^{\text{occ}} |\nabla \Psi_i(\mathbf{r})|^2 - \frac{1}{12} \nabla^2 n(\mathbf{r}) - \frac{1}{24} |\nabla n(\mathbf{r})|^2/n(\mathbf{r}) \right] + O(s^4) \quad (9)$$

Taking the second derivative of $n_x^{\text{av}}(\mathbf{r}, \mathbf{r} + s)$ with

respect to s , evaluated at $s=0$, it follows after some algebra that the kinetic energy can be expressed as

$$T_s[n] = T_w[n] + T_p[n] \quad (10)$$

$$T_w[n] = \frac{1}{8} \int d^3r |\nabla n(\mathbf{r})|^2/n(\mathbf{r})$$

$$T_p[n] = \frac{1}{2} \int d^3r \nabla_s^2 n_x^{\text{av}}(\mathbf{r}, \mathbf{r} + s)$$

Here $T_w[n]$ is the Weizsäcker energy and $T_p[n]$ the Pauli energy. The Pauli energy is frequently less than half the Weizsäcker energy and an approximation to $T_p[n]$ only may be more efficient than an approximation to the total kinetic energy [8]. Note that $T_w[n]$ appears in a natural way in this expression. Through Eq. (10) the Pauli energy is expressed in terms of the spherical average of the exchange hole, and hence a good approximation to the exchange hole should give a good approximation to the Pauli energy. It is, however, important to note that the Pauli energy depends only on the curvature of the exchange hole at the centre of the hole, $s=0$. An accurate representation of the curvature is therefore essential for a good approximation of the Pauli energy.

Writing the kinetic energy in the form of Eq. (10) has a number of advantages. The Weizsäcker term, for example, gives the correct singularity in the first functional derivative of the kinetic energy at the centre of a coulomb potential, which many other approximations fail to give [9].

3. Relevant properties of the exchange hole

Any approximation to the exchange hole must satisfy as many of the properties of the exact hole as can be accommodated. The approximation discussed in this paper satisfies the following conditions.

1. From eqns (6) and (7) it follows that the exchange hole satisfies the sum rule [2]

$$\int d^3s n_x(\mathbf{r}, \mathbf{r} + s) = -1 \quad (11)$$

$$4\pi \int ds s^2 n_x^{\text{av}}(\mathbf{r}, \mathbf{r} + s) = -1$$

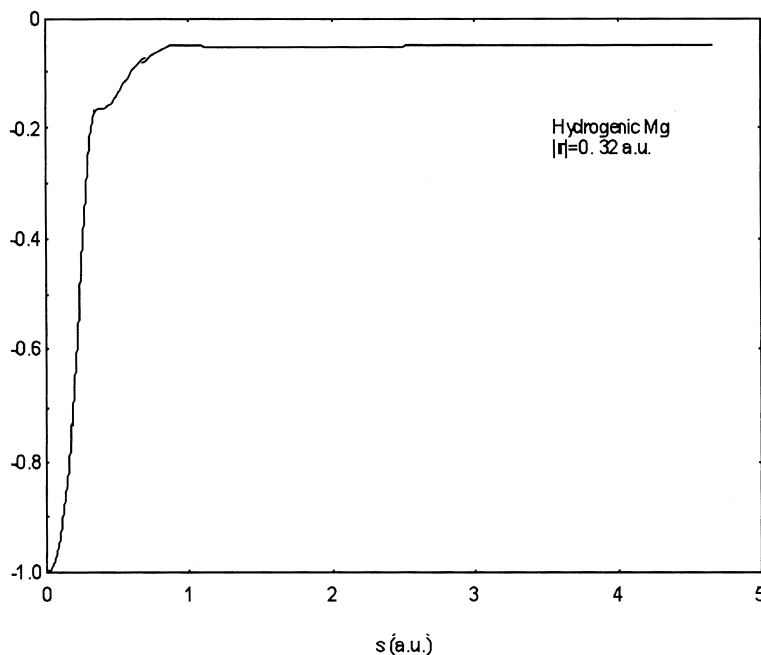


Fig. 1. $n_x^{\text{av}}(\mathbf{r}+s)/n_x(\mathbf{r}+s)$ for hydrogenic Mg centred at $|\mathbf{r}|=0.32$ a.u.

2. When s tends to infinity the exchange hole becomes proportional to $n(\mathbf{r}+s)$ [9]

$$n_x(\mathbf{r}, \mathbf{r}+s)_{s \rightarrow \infty} \rightarrow [n^{N-1}(\mathbf{r})/n(\mathbf{r}) - 1]n(\mathbf{r}+s) \quad (12)$$

where $n^{N-1}(\mathbf{r})$ is the density of an $N-1$ electron system or a linear combination of the ground-state charge densities if the $N-1$ electron system is degenerate. For the spherical average of the exchange hole, $n(\mathbf{r}+s)$ is simply replaced by $n^{\text{av}}(\mathbf{r}+s)$. The property implied by Eq. (12) is illustrated in Fig. 1 for an Mg atomic configuration. The charge densities in this paper were constructed from hydrogenic wave functions for non-interacting N -electron systems. The strength of the central potential and the charge configuration follows from the atomic symbol. Since $n_x(\mathbf{r}+s)$ is non-positive, Eq. (12) implies that the charge density of the $N-1$ electron system is always less than or equal to the charge density of the N electron system at the same point in space when the two systems have the same external potential. This also follows from Eq. (8).

3. A series expansion of $n_x^{\text{av}}(\mathbf{r}+s)$ in s only contains even order terms.
 4. The equation $n_x(\mathbf{r}+0) = -1/2n(\mathbf{r})$ holds (from the definition of n_x).

4. An approximate exchange hole

Since the Fermi energy can be expressed in terms of the spherical average of the exchange hole, it is only necessary to model this average. We propose an approximation of the form

$$n_x^{\text{av}}(\mathbf{r}, \mathbf{r}+s) = n^{\text{av}}(\mathbf{r}+s)f([n^{\text{av}}]; \mathbf{r}, s) \quad (13)$$

The function f must then satisfy the following conditions.

1. $f([n^{\text{av}}]; \mathbf{r}, 0) = 1$ [2].
2. $f([n^{\text{av}}]; \mathbf{r}, s) \rightarrow \text{constant}$ as $s \rightarrow \infty$.
3. A series expansion of f in terms of s may only have terms even in s .
4. Since the sum rule must be satisfied for the density $n(\mathbf{r})$ it must also be satisfied for the uniformly scaled density $n_\lambda = \lambda^3 n(\lambda\mathbf{r})$. This implies that $f([n_\lambda]; \mathbf{r}, s) = f([n]; \lambda\mathbf{r}, \lambda s)$ [9].

As a first attempt we take

$$f(\mathbf{r}, s) = \exp[-\beta(\mathbf{r})s^2 g(n^{\text{av}}, \nabla_s n^{\text{av}})] \quad (14)$$

$$g(n^{\text{av}}, \nabla_s n^{\text{av}}) = n^{\text{av}}(\mathbf{r}+s)^{2/3} (1 + c_1 \alpha(\mathbf{r}) / \{1 + c_2 \sinh^{-2}[\alpha(\mathbf{r})]\})$$

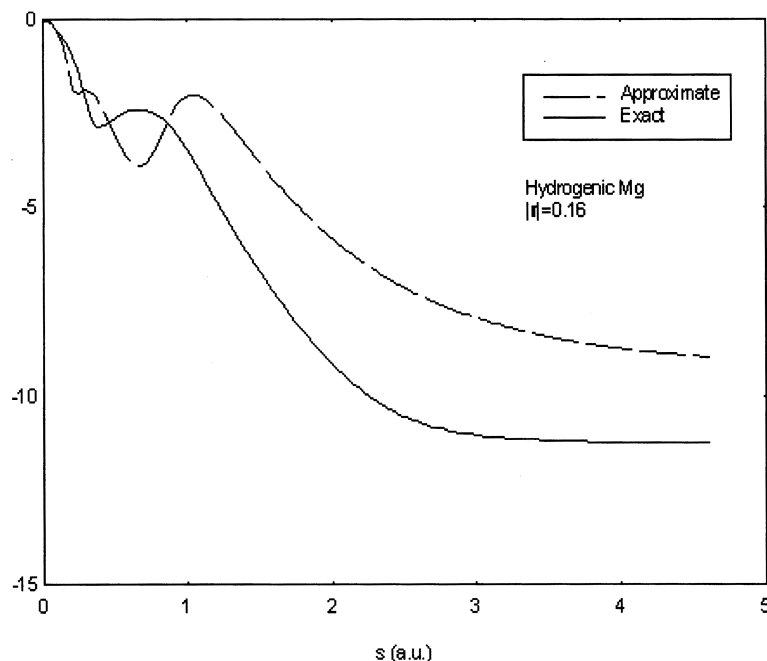


Fig. 2. $g[n^{\text{av}}]$: approximate and exact for hydrogenic Mg for hole centred at $|r|=0.16$ a.u.

$$\alpha(\mathbf{r}) = |\nabla_s n^{\text{av}}(\mathbf{r})| / n^{\text{av}}(\mathbf{r})^{4/3}$$

The constants c_1 and c_2 are determined by fitting the Pauli energy for a number of model systems. This form for the function $f(\mathbf{r}, s)$ (Eq. (14)) becomes constant for large s for densities that decay exponentially, as is the case for any finite system [10]. This is illustrated in Fig. 2.

For this approximation to the exchange hole, the kinetic energy is given by Eq. (4). The function $\beta(\mathbf{r})$ is determined by demanding that the model exchange hole satisfies the sum rule, Eq. (11). For a two-electron system the spherically averaged exchange hole reduces to Eq. (13) with $f(\mathbf{r}, s)=1$. That implies that $\beta(\mathbf{r})=0$ for all \mathbf{r} and from Eq. (4) the Pauli energy is zero. Since the total kinetic energy for a two-electron system is contained in the Weizsäcker term, the kinetic energy is given exactly in this case. For a one-electron system, there exists no exchange hole. However, a sum rule is still satisfied for $\beta(\mathbf{r})=0$ and the total energy is once again given exactly by the Weizsäcker term. For a homogeneous electron gas, the gradient of the charge density is zero. Only the term depending on n^{av} remains in the function g . The

Weizsäcker term is zero and the Pauli term reduces to an integral over $n^{5/3}$. The prefactor, however, is too large and overestimates the correct energy by 3%.

In Fig. 2 the exact and approximate $g(n^{\text{av}})$ only matches well near the origin, $s=0$. Since the Pauli energy is determined by the curvature of $n_x^{\text{av}}(\mathbf{r} + s)$ at the centre of the hole, the total kinetic energy is nevertheless quite accurate in this instance (see Table 1).

Table 1

Percentage error for the kinetic energy for hydrogenic models of atoms^a

Atom	%Error
Be	10.78
Ne	-1.5
Mg	0.64
Ar	-0.49
Ca	0.14
Zn	-3.27
Kr	-1.32
Sr	-0.32
Pd	0.50
Cd	1.29

^a Eq. (14): $c_1 = 77.5$ and $c_2 = 100.0$.

5. Results

The results in Table 1 show a scattering in the accuracy of the approximation, Be being the worst example at a percentage error of 10.7%. This is rather disappointing since Be is a light atom with only four electrons and the approximation is exact for one- and two-electron systems.

Exact kinetic energies and charge densities were generated for independent-electron hydrogenic models of atoms for which wave functions are known analytically. Although these are not accurate models of the physical systems, the kinetic energy is a functional of the charge density [2,3] and the exact functional is valid for these systems. Any approximation must therefore also work well for the systems. The parameters ($c_1=77.5$, $c_2=100.0$) were obtained through a fit to the exact kinetic energy of closed-shell atoms ranging from He to Ra. Apart from Be, the results are of the same order of accuracy as given by the semi-local approximations discussed in Ref. [7]. The approximation discussed in this paper is still not sufficiently accurate for performing independent calculations.

6. Summary and conclusions

An approximate free fermion kinetic non-local energy functional has been constructed from an

approximation to the density functional exchange hole. Reasonable results are obtained for model calculations, but the accuracy of the approximation is not good enough for use in independent calculations.

The approximation to the exchange hole in the form $n_x^{\text{av}}(\mathbf{r}+s) = -1/2n^{\text{av}}(\mathbf{r}+s)f([n^{\text{av}}];\mathbf{r},s)$ suggests that other forms of the function $f([n^{\text{av}}];\mathbf{r},s)$, with the properties listed below Eq. (13), could be explored.

Since the exchange energy can be expressed in terms of the spherical average of the exchange hole [2,3], the approximations Eq. (13) and Eq. (14) can be used to approximate the exchange energy and potential. This will be part of a future study.

References

- [1] P. Hohenberg, W. Kohn, *Phys. Rev. B*, 136 (1964) 864. W. Kohn, L.J. Sham, *Phys. Rev.*, 140 (1965) A1133.
- [2] R.G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989.
- [3] R.M. Dreizler, E.K.U. Gross, *Density Functional Theory*, Springer-Verlag, Berlin, 1990.
- [4] C.F.V. Weizsäcker, *Z. Phys.* 96 (1935) 431.
- [5] A.E. Depristo, J.D. Kress, *Phys. Rev. A* 35 (1987) 438.
- [6] H. Lee, R.G. Parr, *Phys. Rev. A* 44 (1991) 768.
- [7] D.J. Lacks, R.G. Gordon, *J. Chem. Phys.* 100 (1993) 4446.
- [8] C. Herring, *Phys. Rev. A* 34 (1986) 2614.
- [9] C. Herring, *Phys. Rev. A* 34 (1986) 2614.
- [10] D.P. Joubert, M.B. Tchoula Tchokonte, to be published.