A gradient expansion of the electronic current in the electron density is used to obtain expressions for the magnetic susceptibility and chemical shielding. The first term in the expansion is the Thomas Fermi expression. All succeeding terms diverge for both properties. A renormalized functional is used which removes the divergences and gives asymptotic diamagnetism. A single parameter which depends linearly on the number of electrons gives all heavy rare gas susceptibilities to within 1% of exact calculation using the same electron density. Similar results are found for the chemical shielding. Susceptibility and shielding calculations for the helium dimer and the hydrogen molecule in singlet and triplet states are presented. The results are compared with other calculations over a full range of internuclear distances. © 1997 American Institute of Physics. [S0021-9606(97)01642-5]

I. INTRODUCTION

The earliest use of density functional theory as a means of calculating magnetic responses may be found in the work of Cina and Harris. They used an electron gas, or Thomas–Fermi–Dirac, type theory to calculate the magnetic susceptibility tensor of the $^3\Sigma_u$ state of H$_2$. Grayce and Harris then used a similar description of the electrons to calculate the shielding tensor of the same state of H$_2$. The above usage of density functional theory might be called a “pure density functional theory.” That is, responses are obtained from an energy functional by invoking the Hellman–Feynman theorem and taking the appropriate derivatives. This method is in contrast to more recent calculations which solve the Kohn–Sham equations in a vector potential.

In the late 1980s, a direct descendant of the current-density functional theory of Rajagopal and Calloway was advanced. Here it was shown that the energy is a universal function of the density and the gauge invariant quantity $\mathbf{v}$, where

$$\mathbf{v} = \nabla \times \frac{\mathbf{j}_p}{\rho}.$$  

(1)

$j_p$ is the paramagnetic current density, and $\rho$ is the charge density of the electrons. However, practical implementation of this theory in calculating responses has proved elusive.

Recently an entirely different theory of magnetic responses has been developed. It was shown that the magnetic responses are all related to a single tensor response functional. This function is a universal functional of the electron density in the absence of the magnetic field. The functional is, of course, unknown. If one could find reasonable approximations to the functional, all field dependent methods of calculating magnetic responses could be dispensed with. This may well lead to a simpler way of obtaining and understanding the responses.

Locally uniform approximations to the functional have been developed. These were developed by Cina and Harris and Grayce and Harris, in what may be considered precursors to the theory. In reality, their work was a hybrid of ideas. As the functional was meant for application to interacting closed shell systems, additive densities were used. Each atomic density was in the presence of appropriate magnetic fields. Thus, terms in the functional which would make no contribution if the exact nonadditive density were used are manifestly present. This seeming contradiction to the tenets of the general theory is not a surprise. A similar result occurs in all linear responses via density functional theories of interacting closed shell systems: additivity in the presence of external fields is approximately equivalent to nonadditivity in the absence of the fields.

In this article, we attempt to obtain the magnetic susceptibility and the magnetic shielding directly from the total current. The resulting integral expressions, sometimes described as “Biot–Savart integrals,” for the shielding and susceptibility are consequences of linear response theory. That is, the induced current may be looked upon as a response. Hence, according to our theorems, the current is a linear function of the external magnetic field and a function of the unperturbed electron density.

The attempt to construct responses via the induced current has a long history. Such attempts usually involve by-passing perturbation theory or using a Dalgarno–Lewis version of perturbation theory. Indeed there have been attempts to construct currents from a form of quantum hydrodynamics. None of these theories related the current to the unperturbed density, although some came close.
II. THE CURRENT

The current, \( \mathbf{j}(\mathbf{r}) \), is not arbitrary.\(^{10(a)}\) For a bound stationary state, it must be transverse. Since
\[
\nabla \cdot \mathbf{j}(\mathbf{r}) = 0, \tag{2}
\]
we must have
\[
\mathbf{j}(\mathbf{r}) = \nabla \times \mathbf{M}(\mathbf{r}). \tag{3}
\]
In the linear response regime, when the external magnetic field is constant, the most general form of \( \mathbf{M}(\mathbf{r}) \), to within a gradient of a scalar, is
\[
\mathbf{M}(\mathbf{r}) = \mathbf{M}^{(0)}(\mathbf{r}) \mathbf{B} + \mathbf{M}^{(1)}(\mathbf{r}) \times \mathbf{B} + \mathbf{M}^{(2)}(\mathbf{r}) \cdot \mathbf{B}. \tag{4}
\]
\( \mathbf{M}^{(0)} \), \( \mathbf{M}^{(1)} \), and \( \mathbf{M}^{(2)} \) are, respectively, irreducible zero, first and second rank tensors. We may write the shielding and susceptibility tensors in terms of the \( \mathbf{M} \) tensors through use of the integrals\(^{10(b,c)}\)
\[
X_{\gamma \beta} = -\frac{1}{2} \int d^3 \mathbf{r} \left( \mathbf{r} \times \frac{\partial \mathbf{j}(\mathbf{r})}{\partial \mathbf{B}_\beta} \right)_\gamma, \tag{5}
\]
and
\[
\sigma_{\gamma \beta} = \int d^3 \mathbf{r} \left( \mathbf{r} \times \frac{\partial \mathbf{j}(\mathbf{r})}{\partial \mathbf{B}_\beta} \right)_\gamma. \tag{6}
\]
Substitution of Eq. (4) into Eq. (5) gives a contribution from \( \mathbf{M}^{(1)} \) to \( X \) which is a rank one tensor. However, \( X \) is a symmetric tensor, hence \( \mathbf{M}^{(1)} \) must equal zero.

\( \mathbf{M}^{(0)} \) contributes to the scalar component of both \( X \) and \( \sigma \), as well as the symmetric component of \( \sigma \). \( \mathbf{M}^{(2)} \) contributes to all ranks of both responses.

We now set out to determine the \( \mathbf{M} \) tensor as a functional of the unperturbed electron density. In order to orient ourselves, we begin with the only systems, aside from the noninteracting uniform electron gas, where the current and hence, \( \mathbf{M} \), are known exactly when the magnetic field is constant or due to a nuclear spin. These systems are closed shell atoms, or more generally, any rotationally invariant bound system in a state of zero angular momentum. Here the current is entirely diamagnetic.\(^{10(a)}\) That is, in the gauge where
\[
\nabla \cdot \mathbf{A}(\mathbf{r}) = 0, \tag{7}
\]
and, e.g.,
\[
\mathbf{A}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times \mathbf{r}, \tag{8}
\]
the current is, in units where all constants are set equal to one,
\[
\mathbf{j}(\mathbf{r}) = -\mathbf{A}(\mathbf{r}) \rho(\mathbf{r}). \tag{9}
\]
The density, \( \rho(\mathbf{r}) \), is the number density of the electrons. Thus,
\[
\mathbf{j}(\mathbf{r}) = \mathbf{B} \times \nabla \mathbf{M}^{(0)}(\mathbf{r}). \tag{10}
\]
From Eqs. (9) and (10), we may determine the scalar, \( \mathbf{M}^{(0)}(\mathbf{r}) \), namely,
\[
M^{(0)} = \frac{1}{2} \int d^3 \mathbf{r}' \rho(\mathbf{r}'). \tag{11}
\]
Now the scalar susceptibility and shielding are given, respectively, by
\[
X = -\int d^3 \mathbf{r} M^{(0)}(\mathbf{r}), \tag{12}
\]
and
\[
\sigma = 8\pi M^{(0)}(\mathbf{r}). \tag{13}
\]
In terms of the density, we have the well known results,\(^{10}\)
\[
X = -\int_0^\infty drr^2 \rho(r) \tag{14}
\]
and
\[
\sigma = 8\pi \int_0^\infty drr^2 \rho(r). \tag{15}
\]
As mentioned above, our starting point is the locally uniform electron gas model. Here, as we shall see, both the current and \( \mathbf{M}^{(0)}(\mathbf{r}) \) are local functions of the density. Hence, by comparing Eq. (13) in the local electron gas limit with Eq. (15), we see a failure of the local theory. The exact diamagnetic \( \mathbf{M}^{(0)}(\mathbf{r}) \) is nonlocal. \( \mathbf{M}^{(0)}(\mathbf{r}) \), hence the shielding, is an integral over all space. The shielding in the local electron gas theory depends on the density at the nucleus \((r=0)\). Thus, it should come as no surprise that a purely local theory fails to predict shieldings well while giving reasonable susceptibilities. Nor should we be surprised if a “corrected” local theory requires different \( \mathbf{M}^{(0)} \) functional for shieldings and susceptibilities.

III. THE GRADIENT EXPANSION OF THE CURRENT

The problem is how to obtain the current as a functional of the density. We shall assume that the current is that which arises from the solutions of the Kohn Sham equations in the presence of a vector potential.\(^{3c,12}\) The current we construct is not exact. If we use the Hellmann–Feynman theorem to derive the current from the energy functional, there are additional terms.\(^7\) The present approximation is the basis of the original work of Harris and Cain\(^{13}\) and the path integral theory of Harris and Pratt.\(^{12}\) The situation is not unlike the so-called “adiabatic approximation” in time-dependent density functional theory.\(^{14}\)

Given the above approximation, we may express the many electron currents for a closed shell system in terms of the propagator of a single electron in a scalar potential, \( V(\mathbf{r}) \), and vector potential, \( \mathbf{A}(\mathbf{r}) \).\(^1\) Namely,
\[
\mathbf{j}(\mathbf{r}) = -\frac{2}{2\pi i} \int_{-\infty - i\gamma}^{\infty - i\gamma} dt \lim_{\epsilon \to 0^+} \left[ \frac{1}{2i} (\nabla' - \nabla) + \mathbf{A}(\mathbf{r}) \right] \times \langle \mathbf{r} | e^{-iHt} | \mathbf{r}' \rangle, \tag{16}
\]
where
\[
\langle \mathbf{r} | \mathbf{r}' \rangle = \langle \mathbf{r} | e^{-i\mathbf{H}t} | \mathbf{r}' \rangle. \tag{17}
\]
is the single electron propagator. \( H \) is the single electron Hamiltonian in the presence of a scalar potential, \( V(\mathbf{r}) \), and vector potential, \( \mathbf{A}(\mathbf{r}) \). The density, \( \rho(\mathbf{r}) \), is also given by an integral over the propagator:\(^{15(a), (b)}\)

\[
\rho(\mathbf{r}) = \frac{2}{2\pi i} \int_{-\infty}^{\infty} \frac{dt}{i} e^{-i\mathbf{r} \cdot \mathbf{r}_0} \langle \mathbf{r} | e^{-iHt} | \mathbf{r}' \rangle.
\]

Obtaining reasonable approximations for the propagator may be carried out via a generalization of the method of Makri–Miller.\(^{16}\) We begin with the anzatz

\[
\langle \mathbf{r} | e^{-iHt} | \mathbf{r}' \rangle = e^{iW_0(\mathbf{r}, t)} e^{i\int (r-r')^2/2}.\]

The dependence of \( W \) on \( r' \) is implicit. In the weak field limit, we write \( W \) as

\[
W(\mathbf{r}, t) = \mathbf{B} \cdot \mathbf{r}^2 + W_0(\mathbf{r}, t) + W_1(\mathbf{r}, t).
\]

\( \mathbf{B} \cdot \mathbf{r}'/2 + W_0(\mathbf{r}, t) \) represent the propagator when, to lowest order, there is no coupling between the magnetic field and the scalar potential.\(^{17}\) \( W_1(\mathbf{r}, t) \) represents the coupling to first order in the field. \( W_0(\mathbf{r}, t) \) has been calculated by Makri and Miller.\(^{16}\)

We shall obtain an equation for \( W_1(\mathbf{r}, t) \) by substituting Eq. (19) into the time-dependent Schrödinger equation and linearizing in the magnetic field. The resulting equation for \( W_1(\mathbf{r}, t) \) is

\[
-\frac{\partial W_1(\mathbf{r}, t)}{\partial t} - (r-r') \cdot \nabla W_1(\mathbf{r}, t) + \frac{i}{2} \nabla^2 W_1(\mathbf{r}, t) = \mathbf{B} \cdot \mathbf{r}^2 + \nabla W_0(\mathbf{r}, t).
\]

(21)

\( W_0(\mathbf{r}, t) \) is symmetric in \( \mathbf{r} \) and \( \mathbf{r}' \), and \( W_1(\mathbf{r}, t) \) is antisymmetric in the variables. Upon using this symmetry in the equation for the current, we arrive at the result,

\[
\mathbf{j}(\mathbf{r}) = \frac{2}{2\pi i} \int_{-\infty}^{\infty} \frac{dt}{i} \frac{1}{\sqrt{2\pi t}} e^{iW_0(\mathbf{r}, t)}
\]

\[
\times \lim_{\mathbf{r}' \to \mathbf{r}} \frac{1}{2} (\nabla' - \nabla) W_1(\mathbf{r}, \mathbf{r}' t).
\]

(22)

We have explicitly put in both position variables. The diamagnetic contribution to the current is exactly cancelled by the \( \mathbf{B} \cdot \mathbf{r} \cdot \mathbf{r}'/2 \) term in the propagator.

We now seek a gradient expansion for \( \mathbf{j}(\mathbf{r}) \) in terms of the density. This may be accomplished by expanding both \( W_0(\mathbf{r}, t) \) and \( W_1(\mathbf{r}, t) \) as power series in time, and then eliminating the potential in favor of the density. Thus,

\[
W_0(\mathbf{r}, t) = \sum_{n=2} \sum_{n=2} W_n(\mathbf{r}) t^n,
\]

and

\[
W_1(\mathbf{r}, t) = \sum_{n=3} W_n(\mathbf{r}) t^{n-1}.
\]

The first nonvanishing contribution to \( W_1(\mathbf{r}, t) \) appears at \( t^2 \). Hence, substituting the \( W_0(\mathbf{r}, t) \) power series into Eq. (21) yields

\[
(n-1)W_n + (r-r') \cdot \nabla W_n - i \nabla^2 W_n - \sum_{m=2}^{n} \nabla W_{m} \nabla W_{n-m}
\]

\[
= \frac{i}{2} (r-r') \times \mathbf{B} \cdot \nabla W_0^n,
\]

(25)

where \( n = 3 \cdots \infty \).

The lowest order contribution to the current is \( W_3 \), which yields the current

\[
\mathbf{j}(\mathbf{r}) = \frac{\mathbf{B} \cdot \nabla W_0^n}{12\pi^2(2W_2^n)^{1/2}}.
\]

(26)

Since \( W_0^n = V(\mathbf{r}) \), one can change the current from a function of the potential into the current as a function of density. This is done via the Thomas–Fermi relation,\(^{14}\)

\[
2W_2^n = (\pi \rho)^{2/3}.
\]

(27)

The resulting current is identical to the Thomas–Fermi current derived by Harris and Cina.\(^{12}\)

\[
\mathbf{j}(\mathbf{r}) = \frac{(\mathbf{B} \cdot \nabla \rho)}{12(\pi \rho)^{2/3}}
\]

(28)

Their treatment is equivalent to the present one.

We now extend our treatment to fourth order in time. This gives the first gradient corrections to the Thomas–Fermi current. The relevant part of the propagator is,

\[
e^{iW_0(\mathbf{r}, t) + iW_1(\mathbf{r}, t)} \approx e^{iW_0^n} [1 + i(1^2 W_{1}^n + i^2 W_{2}^n + i^3 W_{3}^n - i^4 W_{4}^n)).
\]

(29)

If we only consider terms which involve third order gradients or lower, then \( W_5^n \) does not contribute. The current is thus,

\[
\mathbf{j}(\mathbf{r}) = \frac{\mathbf{B} \times \nabla W_0^n}{12\pi^2(2W_2^n)^{1/2}} - \frac{\mathbf{B} \times \nabla W_2^2}{48\pi^2(2W_2^n)^{1/2}} + \frac{\mathbf{B} \times \nabla W_2^n}{16\pi^2(2W_2^n)^{1/2}}.
\]

(30)

The Thomas–Fermi relation is used for the last two terms of Eq. (29). The first term of Eq. (29) requires gradient corrections to the density.\(^{18}\)

Instead of writing the current explicitly, we write it in terms of \( M \). It may readily be shown that no irreducible second rank tensor, constructed from two \( \nabla \rho \)’s or from \( \nabla \rho \) alone, will have a nonvanishing curl. Hence, only \( M^{(4)} \) appears to second order in the gradients of the density. It is

\[
M^{(4)} = \frac{\rho^{1/3}}{4(3\pi^2)^{2/3}} \left[ 1 + \frac{1}{3} \frac{\mathbf{x} \cdot \mathbf{x}}{\rho^{2/3}} + \frac{4}{9} \frac{\mathbf{x}^2}{\rho^{2/3}} \right],
\]

(31)

where \( \mathbf{x} = \nabla \rho / \rho^{2/3} \). We can only calculate the scalar component of the magnetic susceptibility and the scalar symmetric component of the chemical shielding. We defer consideration of the tensor term to another article.
Another deficiency of the gradient expansion is the divergence of the terms. If we use the gradient expansion to calculate the magnetic susceptibility, the result diverges. The reason is that atomic and molecular electron densities are exponential at long range. Since \( \frac{1}{r^{7/3}} \) → \( r^{2/3} \) as \( \frac{1}{r^{2/3}} \) does, one integrates over all space, the resulting integral diverges. \( r^{1/3} \) is still finite in this instance; although the decay is not fast enough to recover diamagnetism. This divergence is the same type which appears in gradient calculations of the kinetic energy at sixth order in the dimensionless variable \( u^5 \), and at fourth order for the exchange energy. In the current, the divergence occurs at a lower order because the scale, \( r^{1/3} \), is at a lower power of the density. Similarly, the expression for the shielding in the gradient expansion, Eq. (13), is incorrect because the infinite surface integral has been neglected. We shall return to this point in a little while.

IV. ATOMIC SUSCEPTIBILITIES AND SHIELDINGS

Suppose that we truncate the current at the Thomas–Fermi current. What accuracy can we expect? Cina and Harris performed calculations for susceptibility of the hydrogen atom and the triplet state of hydrogen molecule within the additive density approximation. They called the equivalent term “the direct term.” We performed similar calculations using the exact density of the hydrogen atom: \( e^{-2/\pi} \), and Hartree–Fock densities for helium, neon, argon, and xenon. We have also calculated the shielding using the same approximation for the density. The results are given in Table I. The exact calculation of the diamagnetic susceptibilities and chemical shieldings, using the same densities as those used in the Thomas–Fermi calculations, is presented for comparison.

The Thomas–Fermi results for the susceptibility are within a factor of 2.2 in all cases. For hydrogen and helium, however, Thomas–Fermi overestimates for the remaining atoms the results are too low. The reasons for the trend in the Thomas–Fermi magnetic susceptibility is that the Thomas–Fermi shielding density, where the shielding density is the integrand in the susceptibility integral [Eqs. (12) and (14)], decays far too slowly at long distances, but also is too small at short distances. For hydrogen and helium, the Thomas–Fermi underestimate at short distances is over compensated by the slower decay at long distance. For the heavier elements, the short distance shell behavior is more important, and so the underestimate at short distances is not compensated by the long-term distance behavior. That neon is most accurately represented by the Thomas–Fermi function is simply a manifestation of these two errors approximately canceling.

<table>
<thead>
<tr>
<th>Exact shielding</th>
<th>Exact susceptibility</th>
<th>Thomas–Fermi shielding</th>
<th>Thomas–Fermi susceptibility</th>
<th>TF+grad shielding</th>
</tr>
</thead>
<tbody>
<tr>
<td>H 0.333</td>
<td>-0.500</td>
<td>0.282</td>
<td>-0.958</td>
<td>0.294</td>
</tr>
<tr>
<td>He 1.127</td>
<td>-1.394</td>
<td>1.005</td>
<td>-0.841</td>
<td>1.058</td>
</tr>
<tr>
<td>Ne 10.7</td>
<td>-1.388</td>
<td>5.787</td>
<td>-1.064</td>
<td>6.017</td>
</tr>
<tr>
<td>Ar 22.9</td>
<td>-4.34</td>
<td>10.28</td>
<td>-2.576</td>
<td>11.96</td>
</tr>
<tr>
<td>Xe 106.2</td>
<td>-9.00</td>
<td>31.67</td>
<td>-4.308</td>
<td>32.8</td>
</tr>
</tbody>
</table>

FIG. 1. The magnetic susceptibility density of helium. The exact susceptibility density is shown. The density is from the wavefunctions in Ref. 20.

FIG. 2. The modified magnetic susceptibility density of helium. The susceptibility density from the modified function is shown. The density is from the wavefunctions in Ref. 20.

FIG. 3. The magnetic susceptibility density of neon. The exact susceptibility density is shown. The density is from the wavefunctions in Ref. 20.
The behavior of the chemical shielding is harder to understand. In a local density functional theory, the shielding is a functional of the density at the origin alone, whereas in exact diamagnetism, the shielding still involves an integral over all space. The inconsistency here may be an indication that a local density functional theory cannot represent the chemical shielding accurately, or it could mean that different functional are needed to represent the shielding.

As discussed earlier, the gradient expansion for the magnetic susceptibility diverges. The gradient expansion for the shielding also diverges. However, the divergence appears in the infinite surface terms which must sum to zero. The local contribution is finite. Thus, we may consider gradient corrections to the Thomas–Fermi if we only keep the local terms. These terms involve the density, gradient of the density, curvature of the density, etc., all at the nucleus. We have carried out gradient-corrected calculations for the noble gas atoms. Using the first correction to Thomas Fermi,

$$ M^0 = \frac{\rho^{1/3}}{4(3\pi^2)^{2/3}} \left[ 1 + \frac{4x^2}{27(3\pi^2)^{2/3}} \right]. $$

As may be seen in Table I, the improvement is not great.

To improve on the Thomas–Fermi functional and its gradient corrections as far as the shielding goes, the authors took inspiration from the work of A Becke.\(^{21}\) The crucial idea is that to improve a Thomas–Fermi functional, one should multiply it by a function of the dimensionless variable \(u = \frac{x}{\rho(r)^{1/3}}\), such that in the limit of the gradients going to zero, the Thomas–Fermi functional is recovered, and such that the long-range behavior of the function is exact. Becke constructed an exchange potential in this manner by considering the exact expression for the exchange hole. We shall do the same for the current density. At long ranges, one should not be able to tell the difference between diamagnetism and paramagnetism, as in both cases the density looks the same. The long-range behavior we would like to recover is the one in which \(M^0(0) \to \frac{r}{r^2/2}\). Now the function \(\text{arcsinh}\left[\frac{x}{x}\right] \to r\left[\rho(r)^{1/3}\right]\) and the density becomes exponential at large distances. There are many functions which could reproduce this behavior. The only one which the authors found to be reasonably successful in reproducing both the susceptibility and the susceptibility density was

$$ Q = \sum \rho(r)^{1/3} \left[ 1 + Qx \text{arcsinh}\left[\frac{x}{x}\right] \right]^2. $$

\(Q\) is linear in the number of electrons. Figures 1–4 show how well the modified functional reproduces the exact susceptibility density. It must be pointed out that \(M^{(0)}\) as repre-
sented by Eq. (33) has a serious flaw. It can never give net paramagnetism because it is always positive. This restricted physical behavior is true of the Thomas–Fermi $M^{(0)}$ and its first gradient correction. We must be satisfied with obtaining responses in the region of diamagnetism.

We have used modified functionals to calculate the magnetic susceptibilities and the chemical shielding of hydrogen, helium, and the heavier noble gas atoms. Table I shows the atomic susceptibilities given by the Thomas–Fermi approximation as well as the exact results. As the error by our $Q$ fits are 1% or less, we do not give the $Q$ fits here. The $Q_x$ for hydrogen and helium is different from that for the heavier atoms and is given by 3.92 for hydrogen and 3.41 for helium. We have fit the $Q_x$ of the heavier atoms to a function of the form, $Q_x = 5.0067N^{1.426}$, where $N$ is the number of electrons. Again, $Q_x$ for the three heavier atoms may be fit to a linear function of $N$: $Q_x = 0.0232N + 1.87$. For hydrogen and helium, the values of $Q_x$ are 1.79 and 1.65, respectively.

The modified functional corrects the Thomas–Fermi results for the shielding and its gradient correction as well. The functional requires different values of the parameter than the susceptibility. Also, the $N$ dependence is much stronger than for the susceptibility. This is because the functional does not correctly reproduce the short-range dependence of the susceptibility density. This problem requires a functional which reproduces diamagnetism close to the nucleus. Clearly the values of the parameter $Q$ which generate good values of the shielding for the atoms are those for which cancellation of error occurs.

V. SUSCEPTIBILITIES AND SHIELDINGS FOR $H_2$ AND $(He)_2$

Calculation of susceptibilities and shieldings have also been performed for the hydrogen molecule in both the singlet and triplet states, and for the helium dimer. These calculations were carried out at a variety of internuclear distances, using Thomas–Fermi, gradient-corrected Thomas–Fermi (for the shielding), and modified $M^{(0)}$s.

These results were calculated using Mathematica with input densities from GAMESS. The densities are constructed from finite superpositions of Gaussians. Hence, the cusp condition at the nucleus is poorly satisfied. It is precisely the gradient at the origin which matters in our shielding calculations beyond Thomas–Fermi. The density at the origin is quite good. Instead of using the calculated radial derivative, we impose the radial cusp condition,

$$\frac{d\rho(r)}{dr} \bigg|_{r=0} = -2Z\rho(0),$$

Table III. Magnetic susceptibility of helium dimer.

<table>
<thead>
<tr>
<th>Internuclear distance (Å)</th>
<th>Total (atomic units)</th>
<th>Incremental (atomic units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>-2.643</td>
<td>-1.855</td>
</tr>
<tr>
<td>0.4</td>
<td>-2.332</td>
<td>-1.544</td>
</tr>
<tr>
<td>0.6</td>
<td>-1.824</td>
<td>-1.036</td>
</tr>
<tr>
<td>1.0</td>
<td>-1.108</td>
<td>-0.320</td>
</tr>
<tr>
<td>1.5</td>
<td>-0.920</td>
<td>-0.132</td>
</tr>
<tr>
<td>2.0</td>
<td>-0.958</td>
<td>-0.170</td>
</tr>
<tr>
<td>3.0</td>
<td>-1.106</td>
<td>-0.318</td>
</tr>
<tr>
<td>6.0</td>
<td>-0.862</td>
<td>-0.074</td>
</tr>
</tbody>
</table>

FIG. 5. Chemical shielding of helium dimer. The results from the modified (PW), Thomas–Fermi (TF), and gradient-corrected Thomas–Fermi (TF+grad) functions are presented along with the MCSCF results of Van Wullen (Ref. 26). The density has been obtained from GAMESS using a 6-311* basis set.

FIG. 6. Total and incremental magnetic susceptibility of helium dimer. The magnetic susceptibility has been calculated using the modified function referred to in the text. The density has been obtained from GAMESS using a 6-311* basis set.
where \( \rho(r) \) is the radial density; that is, the coefficient of the zeroth rank spherical harmonic in an expansion of the density in spherical harmonics. Direct calculation shows that the angular gradient contributes only a few tenths of a percent in all cases that we have considered.

We now consider our results in light of a few general considerations. The magnetic responses of the hydrogen singlet must be diamagnetic over the full range of internuclear distances. The reason is simply that a two-electron system in its ground state has no nodes.\(^1\)\(^{11}\)\(^{25}\) The triplet state of hydrogen and the He dimer do have nodes, hence may exhibit net paramagnetism in principle. Thus, we expect our results to be particularly poor when there is a region of internuclear distance where net paramagnetism is obtained.

Consider first the He dimer. Van Wullen\(^2\)\(^{26}\) has carried out a careful calculation of the chemical shielding. All three of our functionals give close agreement with Van Wullen’s calculations near the united atom limit. At a large internuclear distance, all of our functionals reach the separated atom limit; a limit which differs somewhat for each functional. However, the separated atom limit is so close for all three functionals because the Thomas–Fermi theory is rather accurate, as illustrated in Table I. As expected, at intermediate distances, none of the shielding functionals exhibit net paramagnetism. The results are presented in Table II and Fig. 5.

The authors are not aware of any calculation of the magnetic susceptibility of the helium dimer. However, Van Wullen\(^2\)\(^{27}\) has commented that he expects the character of the susceptibility of the helium dimer to follow that of the shielding. Thus, in the intermediate region, our calculations may be qualitatively incorrect. (see Table III and Fig. 6). Similar results to those of the helium dimer are found for the shielding of the hydrogen triplet (Table IV and Fig. 7), except that the agreement with the calculations of Grayce and Harris\(^2\) is more qualitative. One should note that the calculation of Grayce and Harris is an electron gas calculation and must be considered to be approximate. This same accuracy is to be found in the calculations of Cina and Harris of the

TABLE IV. Chemical shielding of hydrogen triplet (ppm).

<table>
<thead>
<tr>
<th>Internuclear distance (Å)</th>
<th>Present work modified Thomas–Fermi</th>
<th>Thomas–Fermi with gradients</th>
<th>Grayce &amp; Harris</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>30.9</td>
<td>21.3</td>
<td>21.7</td>
</tr>
<tr>
<td>0.30</td>
<td>26.5</td>
<td>19.1</td>
<td>19.7</td>
</tr>
<tr>
<td>0.40</td>
<td>23.6</td>
<td>17.8</td>
<td>18.2</td>
</tr>
<tr>
<td>0.50</td>
<td>21.5</td>
<td>16.5</td>
<td>17.1</td>
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<tr>
<td>0.60</td>
<td>20.2</td>
<td>15.7</td>
<td>16.4</td>
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<tr>
<td>0.70</td>
<td>19.38</td>
<td>15.29</td>
<td>15.91</td>
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<tr>
<td>0.75</td>
<td>19.14</td>
<td>15.26</td>
<td>15.78</td>
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<tr>
<td>0.80</td>
<td>18.97</td>
<td>15.07</td>
<td>15.69</td>
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<tr>
<td>0.90</td>
<td>18.79</td>
<td>14.98</td>
<td>15.60</td>
</tr>
<tr>
<td>1.00</td>
<td>18.71</td>
<td>14.94</td>
<td>15.57</td>
</tr>
<tr>
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<td>18.39</td>
<td>14.80</td>
<td>15.43</td>
</tr>
<tr>
<td>2.00</td>
<td>19.02</td>
<td>14.64</td>
<td>15.28</td>
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FIG. 7. Chemical shielding of hydrogen triplet. The shielding has been calculated using the modified, Thomas–Fermi (TF), and gradient-corrected Thomas–Fermi (TF+grad) functions. The results of Grayce and Harris (Ref. 2) are shown for comparison. The density has been obtained from GAMESS using a 6–31 + basis set.

TABLE V. Incremental magnetic susceptibility of hydrogen triplet.

<table>
<thead>
<tr>
<th>Internuclear distance (Å)</th>
<th>Present work (atomic units)</th>
<th>Cina &amp; Harris (atomic units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>-1.09</td>
<td>0.788</td>
</tr>
<tr>
<td>0.4</td>
<td>-0.95</td>
<td>0.788</td>
</tr>
<tr>
<td>0.6</td>
<td>-0.80</td>
<td>0.568</td>
</tr>
<tr>
<td>0.8</td>
<td>-0.64</td>
<td>0.568</td>
</tr>
<tr>
<td>1.0</td>
<td>-0.46</td>
<td>0.394</td>
</tr>
<tr>
<td>1.5</td>
<td>-0.07</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.538</td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>0.468</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>0.394</td>
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</table>
magnetic susceptibility of the hydrogen triplet. In this instance our results differ qualitatively from those of Cina and Harris, as may be seen in Table V and Fig. 8.

Our calculations of the magnetic properties of the hydrogen singlet show closer agreement to literature values over the full range of interatomic distances. This agreement is exhibited in Tables VI and VII and Figs. 9–11.

VI. CONCLUSIONS

We have constructed an approximate density functional theory of the magnetic susceptibility and chemical shielding. The theory is based on the Biot–Savart integrals and a density functional expression for the ground state current induced by a homogeneous magnetic field.

The theory is approximate at two levels. First, we have neglected the explicit magnetic field dependent corrections to the Kohn–Sham equations. Their presence is predicted by the theory of Grayce and Harris. We have not investigated the size of this error.

Second, we have expanded the current in a gradient expansion in the unperturbed electron density. This expansion is transverse and gauge invariant. However, as we have discussed earlier, this expansion has huge flaws. To reiterate: a finite sum of gradients can never give pure diamagnetism. The tensor character of the magnetic susceptibility does not appear until fairly high order. The low order terms in the expansion only give diamagnetism, that is, negative magnetic susceptibilities and positive shieldings. And to top it off, for any exponentially decreasing electron density, each term in the magnetic susceptibility and chemical shielding diverges beyond the Thomas–Fermi approximation.

We have attempted to ameliorate at least some of the above problems. We have limited ourselves to calculating the scalar responses. We have attempted to deal with the divergences in two ways. The first way, which holds only for the chemical shift, is to transform the divergences to infinite surface integrals which must sum to zero. Hence, we are left with the shielding as a power series in the density, its gradients, etc., at the nucleus whose shielding is being measured. The second way to correct the current, as well as to give

<table>
<thead>
<tr>
<th>Internuclear distance (Å)</th>
<th>Present work</th>
<th>Zeroka</th>
<th>Internuclear distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>present work</td>
<td>modified</td>
<td>Thomas–Fermi</td>
<td>Thomas–Fermi with gradients</td>
</tr>
<tr>
<td>0.2</td>
<td>−0.543</td>
<td>−0.679</td>
<td>0.53</td>
</tr>
<tr>
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<td>−0.593</td>
<td>−0.693</td>
<td>0.58</td>
</tr>
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<td>0.4</td>
<td>−0.655</td>
<td>−0.806</td>
<td>0.69</td>
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<td>−0.723</td>
<td>−0.893</td>
<td>0.79</td>
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<tr>
<td>0.6</td>
<td>−0.795</td>
<td>−1.026</td>
<td>0.95</td>
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</table>

TABLE VII. Magnetic susceptibility of hydrogen singlet.

TABLE VII. Chemical shielding of hydrogen singlet (ppm).

The theory is approximate at two levels. First, we have neglected the explicit magnetic field dependent corrections to the Kohn–Sham equations. Their presence is predicted by the theory of Grayce and Harris. We have not investigated the size of this error.

Second, we have expanded the current in a gradient expansion in the unperturbed electron density. This expansion is transverse and gauge invariant. However, as we have discussed earlier, this expansion has huge flaws. To reiterate: a finite sum of gradients can never give pure diamagnetism. The tensor character of the magnetic susceptibility does not appear until fairly high order. The low order terms in the expansion only give diamagnetism, that is, negative magnetic susceptibilities and positive shieldings. And to top it off, for any exponentially decreasing electron density, each term in the magnetic susceptibility and chemical shielding diverges beyond the Thomas–Fermi approximation.

We have attempted to ameliorate at least some of the above problems. We have limited ourselves to calculating the scalar responses. We have attempted to deal with the divergences in two ways. The first way, which holds only for the chemical shift, is to transform the divergences to infinite surface integrals which must sum to zero. Hence, we are left with the shielding as a power series in the density, its gradients, etc., at the nucleus whose shielding is being measured. The second way to correct the current, as well as to give

<table>
<thead>
<tr>
<th>Internuclear distance (Å)</th>
<th>Thomas–Fermi with gradients</th>
<th>Zeroka</th>
</tr>
</thead>
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<tr>
<td>present work</td>
<td>Thomas–Fermi</td>
<td></td>
</tr>
<tr>
<td>modified</td>
<td>Zeroka</td>
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</tr>
<tr>
<td>0.90</td>
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<td></td>
</tr>
<tr>
<td>1.0</td>
<td>24.98</td>
<td>19.49</td>
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<tr>
<td>1.5</td>
<td>22.87</td>
<td>17.9</td>
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<td>2.0</td>
<td>22.1</td>
<td>22.16</td>
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diamagnetism asymptotically, is to modify the current functional using ideas developed by Becke. Both of the above methods are still incapable of giving net paramagnetism. In spite of the failings of the approximations, we have shown that a single parameter modified functional, linear in the number of electrons, is capable of giving magnetic susceptibilities and chemical shieldings of the rare gas atoms to within 1% of the best calculated values.

Our calculations on the two states of the hydrogen molecule and of the helium dimer show that we can obtain qualitative accuracy for hydrogen and helium chemical shifts when the system is not paramagnetic or near paramagnetic. The calculations of the magnetic susceptibility show that we can obtain qualitatively accurate results for at least one system which is always diamagnetic: H₂. This reinforces the idea that our method in its present form will work best for molecules which are not paramagnetic or nearly so.

The current is a strongly nonlocal functional of the density. The shielding and the susceptibility measure different aspects of this functional in physical space. It is remarkable that such simple, highly local functionals of the density give such good results in the regions of a priori applicability.

We are in the process of mitigating the titanic shortcomings of the theory. We believe that we do not have to recapitulate 25 years of density functional theory history in order to obtain magnetic responses of chemical accuracy. Indeed, we have recently calculated the hydrogen shieldings of a number of small molecules using the new theory.

ACKNOWLEDGMENTS

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27 C. Van Wullen (private communication).