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Nonlocal-density approximation for exploring kinetic energy anisotropies

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A general procedure for the extraction of directional kinetic energies and Compton profiles exclusively from *total* molecular electron densities has been developed within the nonlocal-density approximation. The estimation of directional kinetic energies and Compton profiles requires the computation of an average electron density $\bar{\rho}(r)$. However, the kinetic energy anisotropy can be evaluated easily by integrating simple functions of electron density and their partial derivatives. The procedure has been tested for the H_2 molecule, where good agreement is found with the results obtained directly from the corresponding wave functions.

I. INTRODUCTION

Several studies emphasizing the significance of the kinetic energy and its directional components in the molecular bonding process[1-6] have been reported in the past 25 years or so. In 1962, Ruedenberg[1] presented arguments to substantiate his claim that chemical bond formation may be interpreted as a result of the *lowering* of kinetic energy, utilizing the "promotional state" of atoms as a reference. Bader and Preston[2] criticized this approach for its use of "unreal and imprecisely defined state of a system." Alternatively, they introduced an entity termed *kinetic energy density* $K(\mathbf{r})$ for assessing the role of kinetic energy T in the bond formation and discussed its physical meaning,

$$K(\mathbf{r})=-\tfrac{1}{4}\nabla^2\rho(\mathbf{r})+\tfrac{1}{8}\sum_i |\nabla\rho_i(\mathbf{r})|^2/\rho_i(\mathbf{r}) , \tag{1}$$

$$\int K(\mathbf{r})d\mathbf{r}=T , \tag{2}$$

where the electron density $\rho(\mathbf{r})$ has been expressed in terms of natural orbitals $\{\phi_i(\mathbf{r})\}$

$$\rho(\mathbf{r})=\sum_i n_i\phi_i^*(\mathbf{r})\phi_i(\mathbf{r})=\sum_i n_i\rho_i(\mathbf{r}) , \tag{3}$$

instead of the most general expression

$$\rho(\mathbf{r})=\sum_{i=1}^{N}\langle\delta(\mathbf{r}-\mathbf{r}_i)\rangle , \tag{4}$$

N being the number of electrons. They compared the cases of H_2 and He_2 focusing on the role played by the kinetic energy during the bond formation. Further studies in this direction were taken up by Wilson and Goddard[3] who christened the nonclassical part of the kinetic energy as the *exchange kinetic energy* T^{ex}:

$$\begin{aligned}T&=T^{\text{cl}}+T^{\text{ex}}\\&=\sum_{i=1}^{n}\langle i\,|\,\hat{t}\,|\,i\rangle\\&\quad+\sum_{(i>j=1)}D_{ij}[2\langle i\,|\,\hat{t}\,|\,j\rangle\\&\qquad-\langle i\,|\,j\rangle(\langle i\,|\,\hat{t}\,|\,i\rangle+\langle j\,|\,\hat{t}\,|\,j\rangle)] ,\end{aligned} \tag{5}$$

where n is the number of orbitals, D the orbital density matrix (not necessarily a unit matrix due to nonorthogonality of the orbitals involved), and $\hat{t}=-\frac{1}{2}\nabla^2$. They concluded, using H_2 as a test case, that T^{ex} plays a crucial role in bonding. More recently, Rama Rao and Chandra[4] examined the bond formation in the weakly bound excited states of HeH^+, and vindicated the statement by Hurley[4] that the behavior of kinetic energy provides a touchstone for the formation of a molecule.

The momentum space offers a more natural ground for the study of the kinetic energy, since the latter is simply the second moment of the electron momentum density $\gamma(\mathbf{p})$:

$$T=\langle p^2/2\rangle=\tfrac{1}{2}\int\gamma(\mathbf{p})p^2d\mathbf{p},\quad p=|\mathbf{p}| . \tag{6}$$

Coulson,[5] in his pioneering works, presented a comprehensive study of the chemical bond in momentum space. He showed that the electron is more likely to move perpendicular to the bond axis with higher velocities. Though this conclusion was reached by simple molecular orbital (MO)—and valence-band (VB)—theoretical considerations, its generality has been verified through numerous studies employing more elaborate computations. Some exceptions to this general observation have recently been noticed by Rawlings and

Davidson[5] who pointed out that the reverse may be the case for σ bonds based on p orbitals. A series of systematic investigations on kinetic energy anisotropies has been carried out by Thakkar, Koga, and co-workers.[6,7] Koga *et al.*[6] studied the connection between the momentum-space anisotropy and bond polarity for diatomics. Sharma and Thakkar[7] analyzed kinetic energy anisotropies in first- and second-row diatomic hydrides and found that nonbonding π orbitals give a large contribution to the anisotropy. A further systematic investigation on kinetic energy anisotropy was recently reported by Thakkar, Sharma, and Koga[7] for the first-row oxides, fluorides, and homonuclear diatomics. They presented detailed tables of orbitalwise breakup of the kinetic energy anisotropy parameter $\alpha=(T_z-T_x)/T$. (In the present work, T_z and T_x denote the parallel and perpendicular components to the bonds axis, respectively, and hence the total kinetic energy T is $2T_x+T_z$.) However, they failed to find definite correlations between α and some familiar molecular properties except for an empirical relation between α and the difference of the numbers of p_σ and p_π electrons.

Surprisingly, very few direct attempts have been reported for establishing links between the electron densities in position and momentum spaces, although the Hohenberg-Kohn theorem guarantees that the ground-state momentum density is a functional of the corresponding position density. Some earlier works[8] used an approach inspired by the semiclassical phase-space considerations. Such an approach leads to a reasonably good estimation of gross properties in the conjugate space. However, it suffers from some important drawbacks. (i) The momentum density thus obtained has a singularity at low momentum value as well as a *wrong* long-range behavior. (ii) This procedure yields *only* spherically averaged momentum density, viz., $\gamma(p)=(1/4\pi)\int\gamma(\mathbf{p})d\Omega p$. The former defect has been remedied[9] by "grafting" the Fourier transform of the square-root of the position density onto the semiclassical momentum density, though it is useful only for spherically symmetric or averaged distributions. Despite these shortcomings, the advantage of the semiclassical approach is that it assumes the knowledge of the electron density only. Other approaches[10] proceed via the Fourier transformation of the Kohn-Sham (KS) orbitals.

A novel attempt for the density-functional calculation of Compton profiles of atoms and molecules was recently reported by Parr, Rupnik, and Ghosh.[11] They introduced a phase-space distribution function $f(\mathbf{r},\mathbf{p})$ which yields a given $\rho(\mathbf{r})$ as well as the correct kinetic energy density $t(\mathbf{r},\rho)$, and obtained its explicit form via the entropy maximization as

$$f(\mathbf{r},\mathbf{p})=\exp[-\alpha(\mathbf{r})-\beta(\mathbf{r})p^2/2] \ . \tag{7}$$

They further introduced a concept of local temperature $T(\mathbf{r})$ defined in analogy with the ideal-gas expression for kinetic energy by

$$\tfrac{3}{2}\rho(\mathbf{r})kT(\mathbf{r})=t(\mathbf{r},\rho) \ . \tag{8}$$

Orbitalwise densities and an assumed form for kinetic energy density were additionally utilized to construct the directional and spherically averaged Compton profiles. They obtained good agreement with the direct results from the Hartree-Fock (HF) wave function (from which the density data were derived). The momentum density extracted from Eq. (7) showed an incorrect asymptotic decay as was the case with the semiclassical method.[8] Nevertheless, the work of Parr *et al.* represents a bold attempt for the construction of directional Compton profiles from the position density.

The aim of the present work is to employ a purely density functional model for the determination of kinetic energy anisotropies. The approach presented here demands only the knowledge of *total* electron densities of atoms or molecules (or solids). No reference to either HF or KS orbitals is made. The background for the present study is provided by the recent application[12] of the nonlocal-density approximation[13,14] (NLDA) to atomic systems, as outlined in the next section. In Sec. III the theory of kinetic energy anisotropies is presented within the NLDA. A special case for two-electron systems is also discussed and tested for the H_2 molecule (Sec. IV) followed by concluding remarks (Sec. V). Atomic units are used throughout this paper.

II. NONLOCAL-DENSITY APPROXIMATION

In what follows, $\Psi(\{\mathbf{r}_i\})$ and $\phi(\{\mathbf{p}_i\})$ denote, respectively, the many-electron wave functions in position and momentum spaces. The corresponding first-order reduced density matrices are designated by $\Gamma(\mathbf{r}\mid\mathbf{r}')$ and $\Gamma(\mathbf{p}\mid\mathbf{p}')$ and the one-electron densities by $\rho(\mathbf{r})$ and $\gamma(\mathbf{p})$.

The first-order reduced density matrix in position space may be written as[13,14]

$$\Gamma(\mathbf{r}\mid\mathbf{r}')=[\rho(\mathbf{r})\rho(\mathbf{r}')]^{1/2}G(\mathbf{r},\mathbf{r}') \ , \tag{9}$$

where $G(\mathbf{r},\mathbf{r}')$ satisfies the condition that

$$G(\mathbf{r},\mathbf{r}')=1 \ . \tag{10}$$

Note that this factorization of $\Gamma(\mathbf{r}\mid\mathbf{r}')$ [Eq. (9)] is exact apart from the problem of the determination of explicit form of $G(\mathbf{r},\mathbf{r}')$. A determination of $G(\mathbf{r},\mathbf{r}')$ is possible by expanding $\Gamma(\mathbf{r}\mid\mathbf{r}')$ and $\rho(\mathbf{r})$ in terms of plane waves[13,14] which leads to

$$G(\mathbf{r},\mathbf{r}')=3j_1(y)/y \ , \tag{11}$$

where $j_n(y)$ is the spherical Bessel function and

$$y=[3\pi^2\rho(\mathbf{r})]^{1/3}\,|\mathbf{r}-\mathbf{r}'| \ .$$

Another approach to connect $\Gamma(\mathbf{r}\mid\mathbf{r}')$ and $\rho(\mathbf{r})$ was developed by Alonso and Girifalco[13] who wrote the spinless second-order density matrix within HF theory as

$$\Gamma^{(2)}(\mathbf{r},\mathbf{r}'\mid\mathbf{r},\mathbf{r}')=\rho(\mathbf{r})\rho(\mathbf{r}')-\tfrac{1}{2}\Gamma(\mathbf{r}\mid\mathbf{r}')\Gamma(\mathbf{r}'\mid\mathbf{r}) \ , \tag{12}$$

and used the definition [analogous to Eq. (9)],

$$\Gamma^{(2)}(\mathbf{r},\mathbf{r}'\mid\mathbf{r},\mathbf{r}')=\rho(\mathbf{r})\rho(\mathbf{r}')[1+C_x(\mathbf{r},\mathbf{r}')] \ , \tag{13}$$

$C_x(\mathbf{r},\mathbf{r}')$ being the correlation factor, known for the case of a homogeneous electron gas,

$$C_x(\mathbf{r},\mathbf{r}')=-\tfrac{9}{2}[j_1(y)/y]^2 \ . \tag{14}$$

Thus, the relation between C and G is furnished [by comparison of Eqs. (11) and (14)] by

$$G(\mathbf{r},\mathbf{r}')=[-2C_x(\mathbf{r},\mathbf{r}')]^{1/2} \ . \tag{15}$$

Relations (9) and (13) with appropriate substitution of G and C from Eqs. (11) and (14), respectively, form the basis of the local-density approximation (LDA). Here it is assumed that the above treatment can be extrapolated to the inhomogeneous electron gas. However, such a choice leads to greatly overestimated values for the kinetic energy, viz.,

$$T[\rho]=T_W[\rho]+T_0[\rho] \ , \tag{16}$$

where T_W is the well-known gradient or Weizsäcker term,

$$T_W[\rho]=\tfrac{1}{8}\int [\,|\nabla\rho(\mathbf{r})|^2/\rho(\mathbf{r})]d\mathbf{r} \ , \tag{17}$$

and T_0 the Thomas-Fermi contribution,

$$T_0[\rho]=\tfrac{3}{10}(3\pi^2)^{2/3}\int [\rho(\mathbf{r})]^{5/3}d\mathbf{r} \ . \tag{18}$$

Yet another serious drawback of the LDA is that it describes the exchange charge density incorrectly. This has been rectified[14] by Alonso and Girifalco and Gunnarsson *et al.* by the introduction "average" density, $\tilde{\rho}(\mathbf{r})$, which satisfies the normalization of the exchange electron density,

$$\int \rho(\mathbf{r}')C_{\tilde{\rho}}^{\mathrm{ex}}(\mathbf{r},\mathbf{r}')d\mathbf{r}'=-1 \ , \tag{19}$$

where, analogous to Eq. (14),

$$C_{\tilde{\rho}}^{\mathrm{ex}}(\mathbf{r},\mathbf{r}')=-\tfrac{9}{2}[j_1(\tilde{y})/\tilde{y}]^2 \ , \tag{20}$$

with $\tilde{y}=|\mathbf{r}-\mathbf{r}'|[3\pi^2\tilde{\rho}(\mathbf{r})]^{1/3}$. Equations (19) and (20) with the above definitions of $\tilde{y}$ constitute the basis of the nonlocal-density approximation (NLDA). The kinetic energy within this approximation estimated from atomic HF electron densities turns out to be comparable to the corresponding true one,[12–14] and is given by

$$T[\rho]=\tfrac{1}{8}\int [\,|\nabla\rho|^2/\rho]d\mathbf{r}+\tfrac{3}{10}\int [(3\pi^2\tilde{\rho})^{2/3}\rho]d\mathbf{r} \ . \tag{21}$$

Gadre and Chakravorty[12] employed Eqs. (19) and (20) and estimated $\tilde{\rho}$ for some atoms *only* from the given electron densities, in contrast to earlier treatments[14] where the pointwise kinetic energy density $t(\mathbf{r})$ was also required. They[12] developed within the NLDA and algorithm for the computation of the autocorrelation function $B(\mathbf{r})$, which is known to be useful for analyzing Compton profiles and provides a link between position and momentum spaces, and used it to extract spherically symmetric momentum densities and Compton profiles from the given $\rho(\mathbf{r})$ *alone.*

III. KINETIC ENERGY ANISOTROPIES AND NONLOCAL-DENSITY APPROXIMATION

A. Formalism

As noted above, the autocorrelation function provides a crucial connection between the position and momentum densities. $B(\mathbf{R})$ is defined as

$$B(\mathbf{R})=\int \Gamma(\mathbf{r}\,|\,\mathbf{r}+\mathbf{R})d\mathbf{r} \ , \tag{22}$$

which can be constructed, within the NLDA, via Eqs. (9) and (11). Thakkar *et al.*[15] have shown that

$$\langle p_z^2\rangle=-B''(0,0,Z)\,|_{Z=0} \ , \tag{23}$$

where the prime means differentiation with respect to Z. Equations (22) and (23) along with the NLDA provides a solution for the kinetic energy anisotropy. From Eqs. (22), (9), and (11), one obtains

$$B(0,0,Z)=3\int [\rho(x,y,z)\rho(z,y,z+Z)]^{1/2}\times[j_1(\tilde{y})/\tilde{y}]d\mathbf{r} \ , \tag{24}$$

where $\tilde{y}=Z[3\pi^2\tilde{\rho}(x,y,z)]^{1/3}$. Now employing the Leibnitz rule for successive differentiation, one obtains

$$B''(0,0,Z)=3\int [\rho(x,y,z)]^{1/2}[a''b+2a'b'+ab'']d\mathbf{r} \ , \tag{25}$$

where

$$a=[\rho(x,y,z+Z)]^{1/2}, \quad b=j_1(\tilde{y})/\tilde{y} \ . \tag{26}$$

It can be readily found that for the limit of $Z=0$,

$$a=[\rho(\mathbf{r})]^{1/2} \ , \qquad a'=\tfrac{1}{2}[\rho(\mathbf{r})^{-1/2}][\partial\rho(\mathbf{r})/\partial z] \ , \tag{27}$$

$$a''=-\tfrac{1}{4}\rho^{-3/2}[\partial\rho(\mathbf{r})/\partial z]^2+(\tfrac{1}{2})\rho^{-1/2}[\partial^2\rho(\mathbf{r})/\partial z^2] \ , \tag{28}$$

$$b=\tfrac{1}{3} \ , \qquad b'=0 \ , \tag{29}$$

$$b''=-\tfrac{1}{15}[3\pi^2\tilde{\rho}(\mathbf{r})]^{2/3} \ . \tag{30}$$

Combination of Eqs. (23), (25), and (27)–(30) yields

$$\langle p_z^2/2\rangle=\tfrac{1}{10}\int \rho(\mathbf{r})[3\pi^2\tilde{\rho}(\mathbf{r})]^{2/3}d\mathbf{r}+\tfrac{1}{8}\int [\partial\rho(\mathbf{r})/\partial z]^2/\rho(\mathbf{r})d\mathbf{r}-\tfrac{1}{4}\int [\partial^2\rho(\mathbf{r})/\partial z^2]d\mathbf{r} \ . \tag{31}$$

This equation provides an approximate method for computation of directional kinetic energy and is valid for molecules and solids as well. The last term on the right-hand side (rhs) vanishes for atoms and molecules for which δ and $\partial^2\rho/\partial z^2\rightarrow 0$ as $|\mathbf{r}|\rightarrow\infty$. The estimates of $\langle p_x^2/2\rangle$ and $\langle p_y^2/2\rangle$ may be similarly obtained by substituting x and y, respectively, in Eq. (31). The most interesting aspect of Eq. (31) is that the directional kinetic energies are made up of two parts: a Weizsäcker-like anisotropic term and a Thomas-Fermi–like isotropic term. In general, an estimation of the kinetic energy components requires the determination of the average electron density $\tilde{\rho}$ via the normalization of the exchange electron density [see Eq. (19)]. However, the kinetic energy anisotropy, defined by $\Delta T=T_z-T_x$, can be approximated by using only the knowledge of $\rho(\mathbf{r})$; the calculation of $\tilde{\rho}(\mathbf{r})$ is no longer needed. From the experience on atomic systems, it is hoped that the total kinetic energies are predictable within the NLDA with a typical error of about 3%. The relative contributions of the Thomas-Fermi–like and Weizsäcker-like terms are typically 40% and 60% for atoms ($4 \leq Z \leq 10$). These trends are expected to be retained within the NLDA estimation of kinetic energy anisotropies as well. In this section, the autocorrelation function has been employed as a connecting link between the kinetic energy anisotropy and electron density in position space. However, the entire algebra could be transcribed in terms of $\Gamma(\mathbf{r} \mid \mathbf{r}')$ as given by Eqs. (9) and (11), leading to the same results.

B. Anisotropic kinetic energy densities, rigorous inequalities, and simplification for two-electron systems

It has been shown in Sec. III A that the kinetic energy components are made up, within the NLDA, of two parts: an isotropic one and a directional one. The corresponding directional kinetic energy densities are furnished by

$$t_z^i = \tfrac{1}{10}[3\pi^2\tilde{\rho}(\mathbf{r})]^{2/3}\tilde{\rho}(\mathbf{r}) \tag{32a}$$

and

$$t_z^a = \tfrac{1}{8}[(\partial\rho/\partial z)^2/\rho] - \tfrac{1}{4}(\partial^2\rho/\partial z^2) , \tag{32b}$$

such that

$$\int [t_z^i(\mathbf{r}) + t_z^a(\mathbf{r})]d\mathbf{r} = T_z , \tag{32c}$$

where the superscripts i and a stand, respectively, for isotropic and anisotropic terms. The second derivative term in Eq. (32b), on integration, does not contribute to T_z for atoms and molecules (see Sec. III A).

A rigorous inequality can be derived on the directional kinetic energy density. Starting with the definition

$$\begin{aligned} |\,\partial\rho/\partial z\,|^2 &= N^2 \left| \frac{\partial}{\partial z} \int \psi^*(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)\psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)d\mathbf{r}_2 \cdots d\mathbf{r}_N \right|^2 \\ &= 4N^2 \left| \int \psi^*(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)[\partial\psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)/\partial z]d\mathbf{r}_2 \cdots d\mathbf{r}_N \right|^2 , \end{aligned} \tag{33}$$

and employing the Cauchy-Schwarz inequality for the rhs, one obtains

$$\tfrac{1}{8}[(\partial\rho/\partial z)^2/\rho] \leq t_z(\mathbf{r}) , \tag{34}$$

where

$$t_z(\mathbf{r}) = (N/2) \int |\,\partial\psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)/\partial z\,|^2 \times d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_N \tag{35}$$

is the "true" kinetic energy density. Similar results can be obtained for the x and y components of the kinetic energy density. Addition of these results, followed by integration, leads to the well-known result derived by the Hoffmann-Ostenhofs[16] that

$$\tfrac{1}{8} \int (\,|\nabla\rho|^2/\rho)d\mathbf{r} \leq T , \tag{36}$$

where T is the true (total) kinetic energy. What has been shown in the present work is that componentwise bounds to kinetic energy, e.g., $T_z \geq (\frac{1}{8})\int[(\partial\rho/\partial z)^2/\rho]d\mathbf{r}$ as well as pointwise bound to directional kinetic energy densities, expressed by Eq. (34), do as well exist.

Further simplification in this treatment is possible for two-electron systems wherein a particular solution to Eq. (19) is provided by the choice $\tilde{\rho}(\mathbf{r}) = 0$ for all $\mathbf{r}$. Hence, for such systems, the z component of the kinetic energy is estimated by

$$T_z = \tfrac{1}{8} \int [(\partial\rho/\partial z)^2/\rho]d\mathbf{r} - \tfrac{1}{4} \int (\partial^2\rho/\partial z^2)d\mathbf{r} . \tag{37}$$

The second term on the rhs of Eq. (37) vanishes for atoms and molecules. It may be noted here that Eq. (37) (along with its x and y analogues) offers an exact treatment[12] for two-electron systems within the molecular orbital (MO) framework.

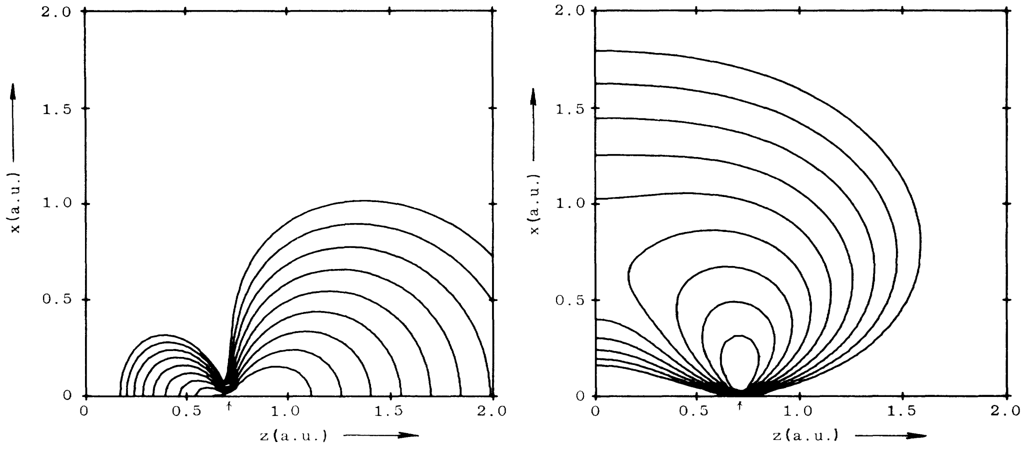
A general formalism for the estimation of kinetic energy anisotropies has so far been presented. The method is general and could be applied to molecules as well as solids. Detailed studies of this type are possible for larger systems. However, a benchmark test of such a formalism is offered by the H_2 molecule. This shall be presented in Sec. IV.

IV. KINETIC ENERGY ANISOTROPIES FOR THE H_2 MOLECULE

The NLDA method for two electron has been put to a test for the H_2 molecule. Since the formulation is exact for the ground states of two-electron systems within MO theory, it was examined using the densities computed within three different models *that go beyond the simple MO framework*.

A. Weinbaum density (Ref. 17)

$$\rho(\mathbf{r}) = \{(1+2cS+c^2)(\phi_a^2+\phi_b^2) + 2[2c+S(1+c^2)\phi_a\phi_b]\}/[(1+c^2)(1+S^2)+4cS] , \tag{38}$$



(a) (b)

FIG. 1. Contours of the directional kinetic energy densities (a) $[(\partial\rho/\partial z)^2/\rho]$ and (b) $[(\partial\rho/\partial x)^2/\rho]$ for the H_2 molecule within the Weinbaum model. See text for details. Successive contour values (starting from the innermost contour) are $2^{-m/2}$ a.u. for $m = 0, 1, 2, \ldots, 8$.

where ϕ_a and ϕ_b are hydrogenic 1s atomic orbitals (AO's) with exponent ζ, c is the weight of the ionic term, and S is the overlap of the AO's. The values (in a.u.) of the parameters employed were $R = 1.42$, $\zeta = 1.193$, and $c = 0.256$. The values of the kinetic energy densities $[(\partial\rho/\partial z)^2/\rho]$ and $[(\partial\rho/\partial x)^2/\rho]$ were generated from $\rho(\mathbf{r})$ given by Eq. (38). Figure 1 displays the contours of these two entities in the positive quadrant of the xz plane (the nuclei are assumed to be located on the z axis). A remarkable fact is revealed by a comparison of these two contour maps, viz., the electron density accumulated in the internuclear region makes very small contribution to T_z, but contributes significantly to T_x. The contributions of this region towards T_z and T_x are 0.012 and 0.226 a.u., respectively, the corresponding "exonuclear" values being 0.263 and 0.202, bringing out slow variation of $\rho(\mathbf{r})$ with respect to z in the internuclear region. This is yet another way of visualizing Coulson's momentum space picture of bond formation referred to in Sec. I. For a comparison, a contour diagram of $[(\partial\rho/\partial x)^2/\rho]$ when an H atom is placed at the nuclear position on positive z axis is depicted in Fig. 2. It may be noticed here that the x component of the molecular kinetic energy density (Fig. 1) shows a close resemblance to Fig. 2. The z component for H atom is obtainable by a 90° rotation of Fig. 2. This component is markedly different from the corresponding molecular one (see Fig. 1) which is a reflection of the lowering of the parallel component upon bond formation stressed in the earlier literature.[1-4] The results of total contributions to T_z and T_x along with the respective true values computed directly from the respective wave functions are shown in Table I. It may be noticed from this table that the components T_z and T_x are underestimated within NLDA by about 5% and 0.2%, respectively, when compared to their true values in conformity with the bounds discussed in Sec. III B. The relative error in $T_z - T_x$ value predicted by the NLDA is about 11%. What is indeed remarkable is that 89% of the total kinetic energy anisotropy for the H_2 molecule is picked by the simple method offered in the present work. The total kinetic energy is underestimated by about 1.6% by the present approach in accordance with the bound (36) due to the Hoffmann-Ostenhofs.[16]

B. Wang density (Ref. 18)

This is also a valence-bond model slightly inferior to the Weinbaum one in that the ionic terms in the latter are absent here. Thus, Eq. (38) holds good here as well with the choice $c = 0$. The optimized values of the orbital exponent and R are 1.1661 and 1.414, respectively. Contour plots of the kinetic energy density components

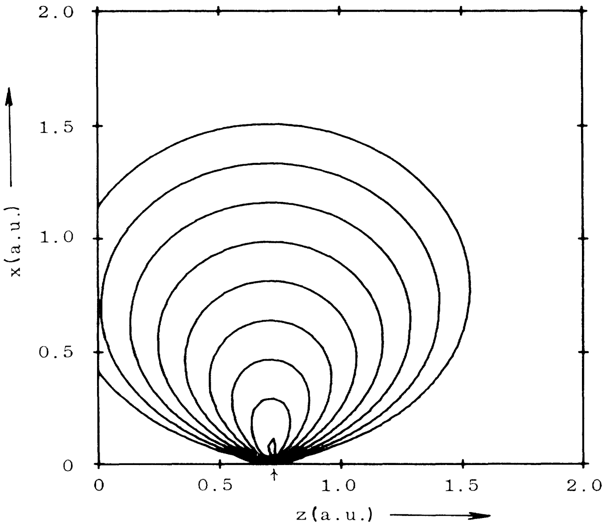


FIG. 2. Contours of $[(\partial\rho/\partial x)^2/\rho]$ for the hydrogen atom, centered at the nucleus on the positive z axis. See text for details. Successive contour values, starting from the innermost, are $2^{-m/2}$ a.u. for $m = 0, 1, 2, \ldots, 8$.

TABLE I. The directional and total kinetic energies, T_z, T_x, $T=T_z+2T_x$, and the kinetic energy anisotropies $\Delta T = T_z - T_x$ for the H_2 molecule within the NLDA along with the corresponding wave-function counterparts (all values in hartrees a.u.).

	T_z		T_x		$-\Delta T$		T	
Density	NLDA	True	NLDA	True	NLDA	True	NLDA	True
Wang[a]	0.269	0.306	0.414	0.417	0.145	0.111	1.097	1.140
Weinbaum[a]	0.275	0.291	0.428	0.429	0.153	0.138	1.131	1.149
Stewart[b]	0.283		0.426		0.144		1.136	1.174

[a] Using the optimized equilibrium values for the VB-type wave functions with and without ionic contributions from Refs. 17 and 18. See text for details.

[b] Employing the electron density from Ref. 19. See text for further details.

show features similar to those exhibited by Fig. 1. The typical errors in T_z, T_x, and T (as predicted by the NLDA turn out to be about 12%, 0.7%, and 0.4%, respectively (see Table I).

C. Stewart-Davidson-Simpson density (Ref. 19)

The most elaborate (and accurate) electron density examined in the present work is due to Stewart *et al.*[19] and bears the form

$$\rho(\mathbf{r}) = (1/2\pi)(2/R)^3 \exp(-\alpha\xi) \sum_{k,j} a_{kj}\xi^k\eta^j \,. \tag{39}$$

This density has been obtained by some rearrangement of an earlier natural spin-orbital expansion due to Davidson and Jones.[20] Here, ξ and η are the usual confocal elliptical coordinates. The results of our NLDA calculations are displayed in Table I. However, no wave-function counterparts were found in the literature for a direct comparison. The total kinetic energy is underestimated here by about 3.2%. The features exhibited by Fig. 1 are also shared by this sophisticated density.

D. Repulsive state

We present here, for a comparison, the plots of the NLDA directional kinetic energy densities for the repulsive ${}^3\Sigma_u^+$ state, within the Wang model, in Fig. 3. Optimal parameter values used here are $R=1.414$ and $\zeta=0.9353$. It may be seen that there is a sizable contribution to T_z from the internuclear region, though the x component does not differ from that for the singlet bonding state within the Wang model (see Fig. 1). However, the NLDA formalism cannot be directly applied to this case since Eqs. (11) and (12) are derived under the assumption of doubly occupied HF orbitals. Though the modification of the theory is not difficult in the present case, we omit the discussion and numerical results. Nevertheless, the comparison of Figs. 1–3 brings out the significant difference of the z component for the attractive and repulsive states.

V. SUMMARY AND CONCLUDING REMARKS

In the present work, the nonlocal-density approximation has been employed for estimating the kinetic energy

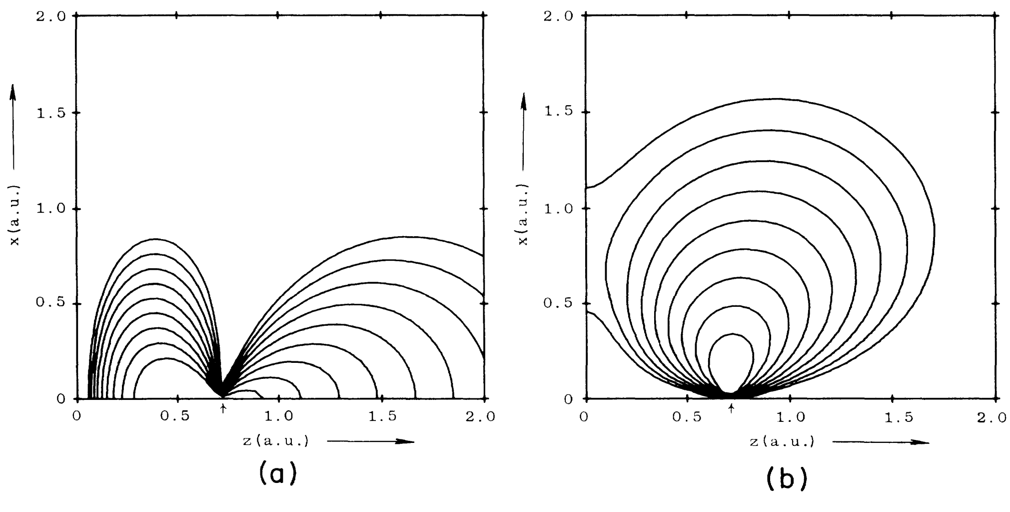


FIG. 3. Contours of (a) $[(\partial\rho/\partial z)^2/\rho]$ and (b) $[(\partial\rho/\partial x)^2/\rho]$ for the repulsive triplet state of the H_2 molecule within the Wang model (refer to text). Contour values are as in Figs. 1 and 2.

anisotropies. The crucial link between the position and momentum spaces is provided here by the autocorrelation function $B(\mathbf{r})$. Directional kinetic energy T_z within the NLDA has two ingredients: an isotropic one, viz.,

$$\tfrac{1}{10}(3\pi^2)^{2/3}\int[\tilde{\rho}(\mathbf{r})]^{2/3}\rho(\mathbf{r})d\mathbf{r}\ ,$$

and an anisotropic one, viz.,

$$\tfrac{1}{8}\int[(\partial\rho/\partial z)^2/\rho]d\mathbf{r}-\tfrac{1}{4}\int(\partial^2\rho/\partial z^2)d\mathbf{r}\ .$$

Any directional kinetic energy could thus be estimated by suitable three-dimensional numerical integrations including those required for the computation of $\tilde{\rho}(\mathbf{r})$. A particularly pleasing situation arises for two-electron systems, for which $\tilde{\rho}(\mathbf{r})=0$, assuring the exactness of the NLDA within MO framework. Pointwise bounds to $t_z(\mathbf{r})$ as well as to its integral T_z have been rigorously derived in the present work. A numerical investigation of the formalism for the case of H_2 molecules employing densities outside the realm of MO theory reveals that it can predict the directional kinetic energies as well as the anisotropies fairly well. Further considerations on the correlation hole are expected to improve the results. The plots of $[(\partial\rho/\partial z)^2/\rho]$ and $[(\partial\rho/\partial x)^2/\rho]$ bring out the regionwise contributions to T_z and T_x are assured to be at least equal to those predicted by the NLDA.

The highlight of the present work for N-electron systems is that the kinetic energy anisotropy $\Delta T=T_z-T_x$ can be predicted by numerical quadrature of the simple functions of the electron density and its partial derivatives: the evaluation of $\tilde{\rho}(\mathbf{r})$ is not required. For isolated molecules, the second derivative term does not contribute, while for solids it does. Thus, the electron density maps obtained by x-ray methods could be utilized for a calculation of the kinetic energy anisotropies. In fact, the entire autocorrelation function $B(\mathbf{r})$ can be determined from an experimental $\rho(\mathbf{r})$ map. This indeed represents a significant development, since, the Compton profile which can be measured directly via the x-ray, γ-ray, and synchrotron-radiation scattering experiments, is simply the Fourier transform of $B(\mathbf{r})$.

The treatment outlined in this paper *does not* require the knowledge of orbitalwise densities. Also, the electron momentum densities extracted from $\rho(\mathbf{r})$ within the NLDA are guaranteed to show proper limiting ($|\mathbf{p}|\rightarrow 0$) as well as asymptotic behavior due to the inclusion of the Weizsäcker term. Such proper behavior is shown neither by the Parr approach[11] nor by the earlier semiclassical[8] treatments. The formalism developed in the present work can be used in the reverse direction as well, enabling an estimation of diamagnetic anisotropy susceptibilities (yet another experimentally measurable quantity) from three-dimensional $B(\mathbf{r})$ or momentum density maps. The NLDA approach, with correlation hole conditions grafted on, if required, thus seems to offer an interconnection between the electron densities in position and momentum spaces.

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