Reduced local energy surface profiles for hydrogen

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Three dimensional molecular reduced local energy error surface profiles are reported. The calculations are carried out for the hydrogen molecule using the Hartree–Fock wavefunctions of Coulson, Goodisman and Kołos and Roothaan. These surfaces provide both a complete and a simple way to interpret *local* errors in these wavefunctions.

1. INTRODUCTION

It is well known that a wavefunction, optimized using the standard variation method to yield the best energy, does not necessarily lead to equally satisfactory values for the expectation values of other observables. (See for example the work of Mukherji and Karplus [1] ; a concise account is given in Pilar [2].) Two factors that are important for an understanding of the preceding comment are as follows. The standard variational procedure tends to optimize the wavefunction in a restricted region of configuration space, which is of course, directly tied to the form of the operators which make up the hamiltonian. For an operator that depends on a region of configuration space different from that emphasized in variational calculations, it is not too surprising that the expectation value of such an operator may not agree with the experimental value. A second and perhaps somewhat more subtle feature of the variational procedure concerns the possible cancellation of errors in energy computations. It is possible that the wavefunction may be inaccurate in the region important for determining the energy, but offsetting errors in different regions of configuration space lead to an overall value of the energy which is very good. For an operator emphasizing a different region, there may no longer be the same cancellation of error, with the obvious result that a less satisfactory value for the expectation value is obtained.

There is one obvious way to examine if the above mentioned factors are important, and this is to explore the *local* behaviour of the wavefunction. This idea has been in the literature for a considerable time. Some years ago Frost [3, 4] considered the problem in the following way. Dividing the usual Schrödinger equation by Ψ leads to

$$E = \frac{(H\Psi)}{\Psi}. \tag{1}$$

If Ψ is exact at *each* point of configuration space, the right hand side of equation (1) should be a constant equal to the exact energy of the system. If a trial

wavefunction ψ is employed, then $(H\psi)/\psi$ is a function of each particle coordinate. Clearly, the constancy of $(H\psi)/\psi$ may be used as a criterion for the accuracy of the trial wavefunction. Frost took the idea one step further and proposed determination of the energy using

$$\epsilon = \frac{(H\psi)}{\psi}, \qquad (2)$$

where a suitable set of representative points in configuration space were selected. Parameters appearing in the trial wavefunction were optimized in a least squares procedure by minimizing the variance of ϵ. A number of authors have taken up this approach [5–20].

2. REDUCED LOCAL ENERGY

The main difficulty associated with the Frost approach is that, for an N electron wavefunction, the dependence of ψ on $3N$ electronic coordinates makes this approach difficult to implement. A simplification of the Frost local energy concept was suggested by Rothstein and co-workers [21, 22]. These authors introduced the notion of a reduced local energy, defined for a system of N ($\geqslant 2$) electrons by

$$E_{\mathrm{L}}(\mathbf{r}_1) = \frac{\int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N) H \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N) \, ds_1 \, d\tau_2 \, d\tau_3 \dots d\tau_N}{\int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N) \, ds_1 \, d\tau_2 \, d\tau_3 \dots d\tau_N}. \qquad (3)$$

For the exact wavefunction, E_{L} defined by equation (3) is a constant for all points in configuration space. Equation (3) has the advantage that interpretation of the local behaviour of Ψ is simplified in comparison to equation (2), however it should be noted that there may be subtle cancellation of inaccuracies arising in equation (3). Equation (3) may be used as a necessary condition for determining the local accuracy of the wavefunction, but it is not a sufficient condition.

The recent work of Cohen and Frishberg [23] and Nakatsuji [24] has shown that a result of the same form as equation (3) holds when Ψ is the Hartree–Fock wavefunction and E is replaced by the Hartree–Fock energy, that is

$$E_{\mathrm{L}}^{\mathrm{HF}}(\mathbf{r}_1) = \frac{\int \Psi_{\mathrm{HF}}^*(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N) H \Psi_{\mathrm{HF}}(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N) \, ds_1 \, d\tau_2 \, d\tau_3 \dots d\tau_N}{\int \Psi_{\mathrm{HF}}^*(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N) \Psi_{\mathrm{HF}}(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N) \, ds_1 \, d\tau_2 \, d\tau_3 \dots d\tau_N}. \qquad (4)$$

Several generalizations and applications employing the reduced local energy, the reduced local energy matrix and the related density matrix equation have recently appeared [25–30].

Since the vast majority of atomic and molecular wavefunctions in the literature are of Hartree–Fock quality, equation (4) should represent a very useful procedure to test the local accuracy of such wavefunctions. Equation (4) has only very recently been utilized to study the local accuracy of wavefunctions. Two of the authors have examined the local behaviour of the Clementi [31], Clementi–Roetti [32] atomic Hartree–Fock wavefunctions and some locally refined wavefunctions [33–35]. A study by Grelland and Almlöf of the local accuracy of the Hartree–Fock wavefunctions for H_2O and CH_4 has just appeared [36]. These authors determined some surface contour maps of the local behaviour of the wavefunctions for these molecules.

3. REDUCED LOCAL ENERGY ERROR PROFILES

The purpose of the present work is to present three dimensional maps of the local behaviour of a molecular wavefunction, using the reduced local energy defined in equation (4) as a measure of the error in different regions of configuration space. Because symmetry will be employed to reduce the coordinate dimensional space from 3 to 2, our profiles are three dimensional in the sense that E_L^{HF} is employed in place of the eliminated angular coordinate. The molecule of interest in this study is hydrogen. Our attention has been focused on this molecule for two reasons. It is a two-electron system, so computations on a large number of points in configuration space are possible without using an excessive amount of computer time. Also, the hydrogen molecule has been well studied in the literature and the present study provides an examination of the local accuracy of some carefully prepared wavefunctions.

The orbital functions that have been examined take the form

$$\psi = \sum_i C_i \xi^{m_i} \eta^{n_i} \exp\left(-\delta\xi\right), \tag{5}$$

where the elliptic coordinates are

$$\xi = \frac{r_A + r_B}{R}, \quad \eta = \frac{r_A - r_B}{R}. \tag{6}$$

R is the internuclear distance and r_A, r_B are the appropriate electron–nuclei distances. δ is a parameter that has been selected to optimize the energy.

The parameters employed in the wavefunction, equation (5). For each wavefunction $\delta = 0.75$ and $R = 1.4\ a_0$.

| Wavefunction	Number of terms	(m_i, n_i) values	Electronic energy/E_h
Coulson [37]	5	(0, 0), (1, 0), (2, 0) (0, 2), (1, 2)	−1·847462
Goodisman [38]	9	(0, 0), (0, 2), (1, 0) (2, 0), (1, 2), (0, 4) (1, 4), (2, 2), (3, 0)	−1·847859
Kołos–Roothaan [39]	9	(0, 0), (1, 0), (2, 0) (0, 2), (1, 2), (3, 0) (4, 0), (2, 2), (0, 4)	−1·847903

Three different Hartree–Fock wavefunctions for hydrogen have been examined. The appropriate values of δ, R, m and n are given in the table. The first wavefunction studied is based on an old calculation, which is primarily of historical interest, made by Coulson in the pre-computer era [37]. Coulson developed several wavefunctions for hydrogen. However, we have only examined his best function which contains five basis terms in the expansion given by equation (5). We have recalculated the Coulson expansion coefficients

C_i using the same values of m_i and n_i which he employed. The refined coefficients have been employed to compute the reduced local energy error profile. The second and third wavefunctions considered represent rather accurate Hartree–Fock descriptions for the energy of the hydrogen molecule [38, 39]. The expansion coefficients were calculated from our own Hartree–Fock program.

To simplify equation (4), we have taken advantage of the cylindrical symmetry and integrated both the numerator and denominator with respect to the angle ϕ. The reduced local energy is now a function of the two elliptic coordinates ξ and η, that is, $E_L^{HF}(\xi, \eta)$. The reduced local energy error surfaces have been constructed with ξ and η the *in-plane* coordinates, and the vertical coordinate represents the absolute value of the electronic contribution to the reduced local energy. The origin for the vertical axis has been set at $1 \cdot 848 E_h$ which represents the absolute value of the Hartree–Fock electronic energy of the hydrogen molecule (to four significant figures). The rest of this paper will be concerned only with the total electronic energy.

The evaluation of the appropriate matrix elements appearing in equation (4) is straightforward, though somewhat more tedious than the determination of the matrix elements required for the evaluation of the Hartree–Fock energy. There is a loss of symmetry which arises because integration over all coordinates is not performed, with the result that the final expressions for the matrix elements are somewhat more involved. All the computations reported were carried out on a Honeywell DPS 8/20 using double precision.

Figure 1 shows the results for the Coulson wavefunction. Figure 1 (*a*) gives an overview of the whole surface and figures 1 (*b*) and (*c*) show cross-sectional cuts along the internuclear axis and perpendicular to the internuclear axis (passing through one of the hydrogen nuclei). The long axis horizontal scale corresponds to three times the H_2 bond length. The short axis scale is based on the same scale. The reduced local energy scale is indicated in
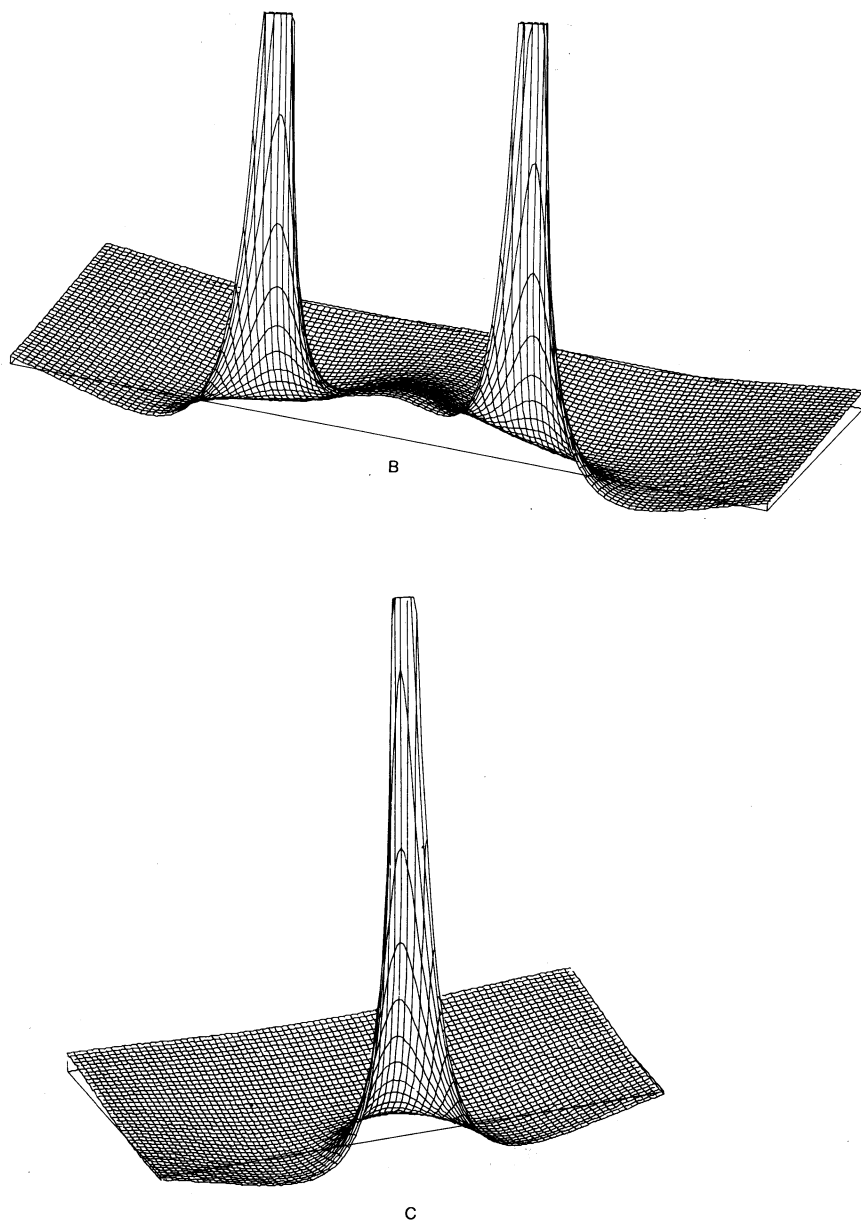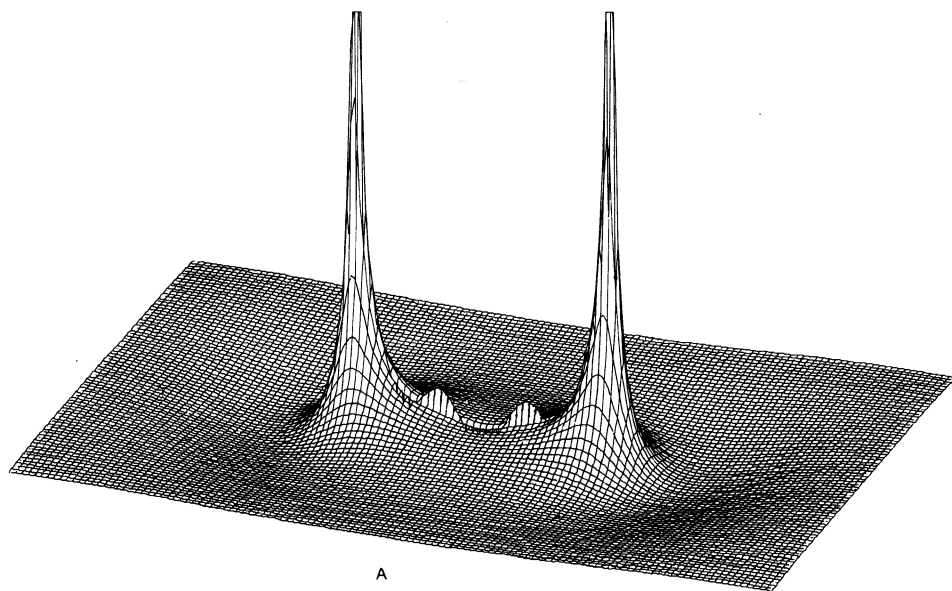

$.2\ E_h$

A

B

C
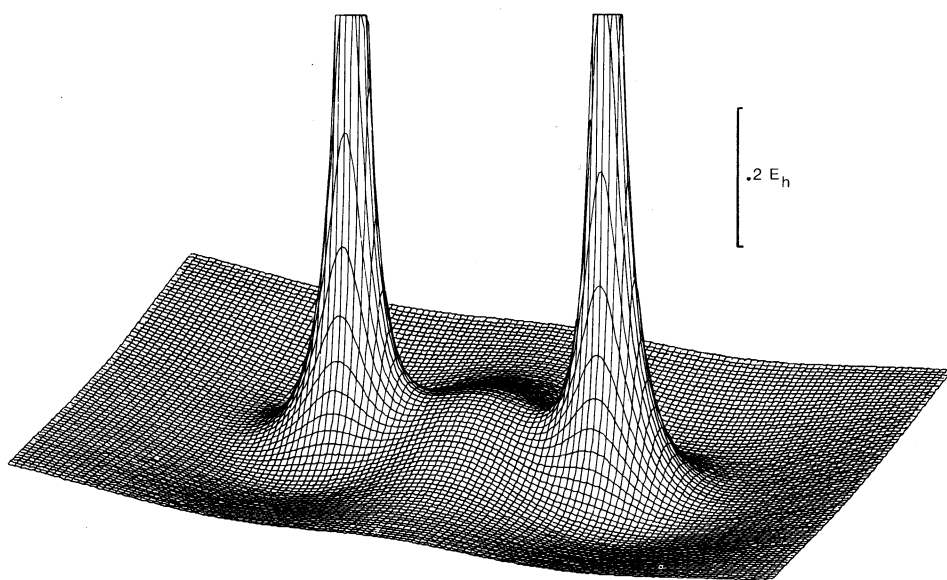
Figure 1.   Reduced local energy error surface for the hydrogen molecule using the Coulson five-term Hartree–Fock wavefunction.   (*a*) shows the whole surface.   The vertical axis represents $|E_\mathrm{L}^{\mathrm{HF}}(\xi, \eta)|$ in E_h.   The elliptic coordinates ξ and η are the other two axes.   The horizontal long axis corresponds to three times the hydrogen bond length.   The horizontal short axis is based on the same scale.   (*b*) shows a cross-sectional cut along the internuclear axis.   (*c*) shows a cross-sectional cut perpendicular to the internuclear axis and passing through one hydrogen atom.   The grid origin is set at $|E_\mathrm{L}^{\mathrm{HF}}| = 1\cdot848\ E_\mathrm{h}$.

figure 1 (*a*). The position of each hydrogen atom is indicated by the two spikes in the figure. The plane defined by the frame in figures 1 (*b*) and (*c*) indicates the absolute value of the *exact* Hartree–Fock electronic energy.

The *exact* Hartree–Fock wavefunction for H_2 would yield a flat plane, since $|E_L^{HF}(\xi, \eta)|$ is a constant independent of ξ and η. The most obvious feature from the figure is that the reduced local energy changes abruptly in the region of each hydrogen nucleus. At each nucleus the reduced local energy becomes infinite. It is also clear from the figure, particularly from the long-axis cross-sectional cut, that E_L^{HF} deviates significantly from a constant value in the region between the two nuclei. This is the region of configuration space which is important for the calculation of most typical expectation values. It should also be noted (see the cross-sectional views) that there are both positive and negative deviations from the constant E^{HF}. Since the total Hartree–Fock electronic energy is obtained by integrating $E_L^{HF}(\xi, \eta)$ multiplied by the ϕ angle averaged electronic density, the positive and negative deviations partly offset each other, with the result that a reasonably accurate value of E^{HF} is obtained. However, this cancellation of errors would not be expected to be equally fortuitous for a wide range of different expectation values.

The second wavefunction examined is due to Goodisman and the reduced local energy error surface is shown in figure 2. The Goodisman function is observed to lead to a much more accurate E_L^{HF} surface, compared to the results obtained from the Coulson wavefunction. A comparison of the long-axis cross sectional cuts (figures 1 (*b*) and 2 (*b*)) shows that the Goodisman E_L^{HF} is better in the important internuclear region. The Goodisman reduced local energy displays some oscillatory behaviour along the internuclear axis. The low point, at the midpoint of the internuclear separation, corresponds to $|E_L^{HF}| = 1\cdot823\ E_h$ and the neighbouring crest corresponds to $|E_L^{HF}| = 1\cdot899\ E_h$. Since the region between the nuclei is important for the determination of the total electronic energy, there is obviously some favourable cancellation of errors of
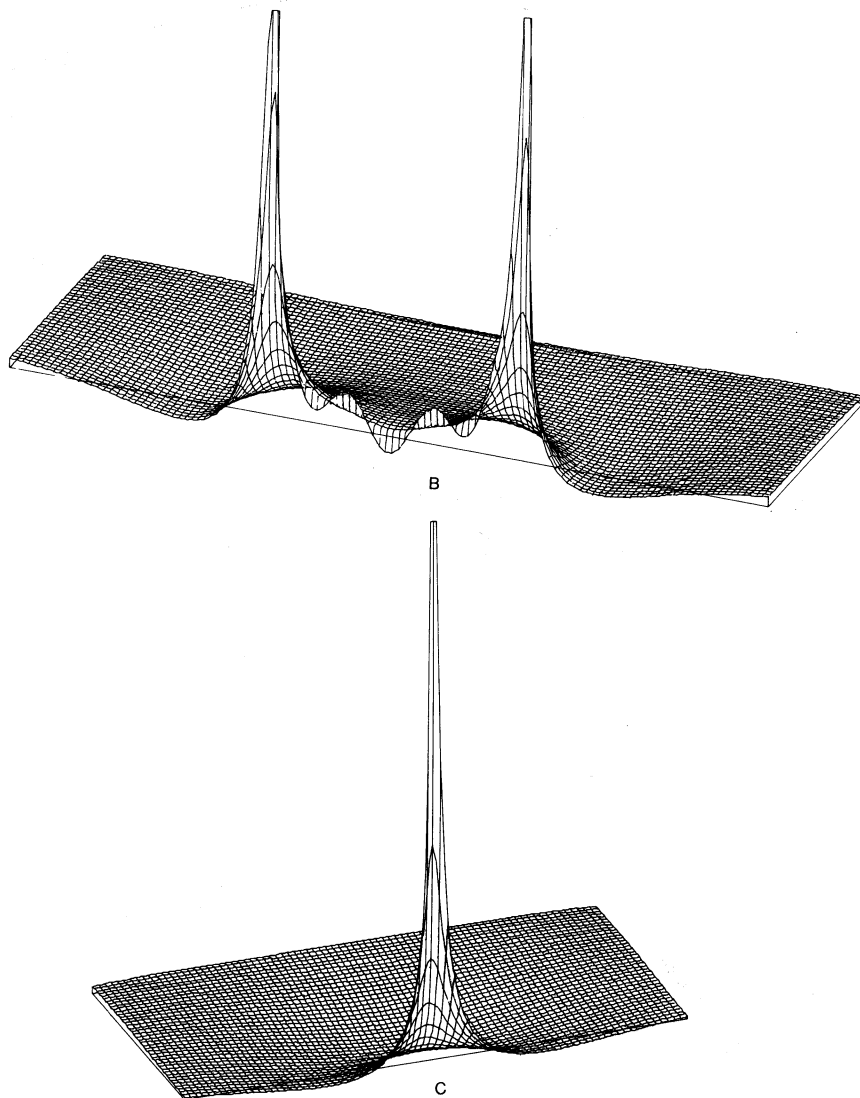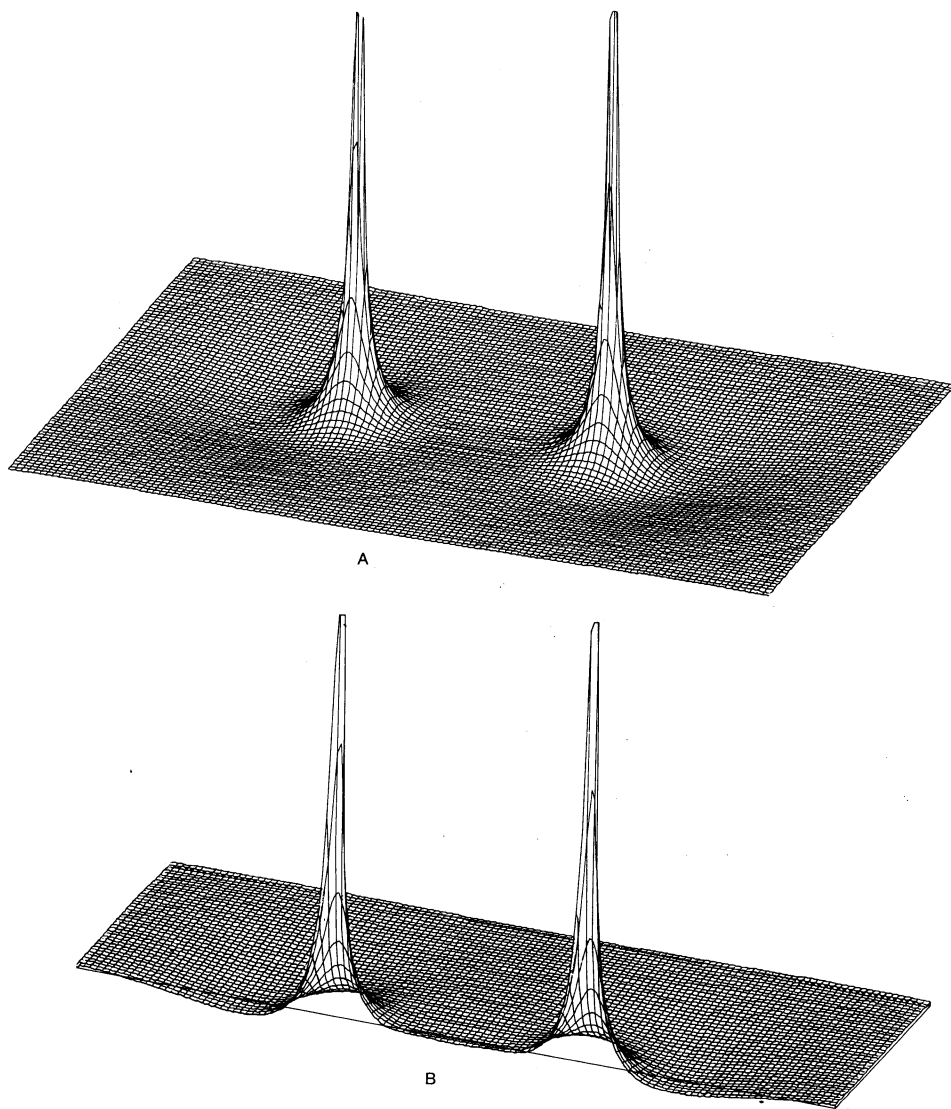

A

Figure 2. Reduced local energy error surface for H_2 using the Goodisman nine-term Hartree–Fock wavefunction. (*a*) is the whole surface ; (*b*) and (*c*), cross-sectional views. The scales are the same as for figure 1.

opposite sign, implicit in the value of E^{HF} obtained with the Goodisman wavefunction.

The third wavefunction examined is a 9-term expansion due to Kołos and Roothaan. These authors have given an extensive number of Hartree–Fock wavefunctions for the hydrogen molecule. We have selected the wavefunction with the same exponential parameter ($\delta = 0.75$) and bond length used by Coulson and Goodisman. The reduced local energy error surface computed from the Kołos–Roothaan wavefunction is shown in figure 3. From figure 3 the Kołos–Roothaan E_L^{HF} surface is observed to be superior to the Goodisman E_L^{HF}

surface. The Kołos–Roothaan $E_L{}^{HF}$ diverges (that is, $E_L{}^{HF} \to -\infty$) at each of the hydrogen nuclei, a feature common to all three wavefunctions investigated. The spikes on the Kołos–Roothaan surface are slightly sharper than the corresponding spikes on the Goodisman surface. The most obvious feature observed from figure 3 (*a*) is the constancy of $E_L{}^{HF}$ everywhere except the two nuclear positions. An indication of how close the flat region corresponds with the *exact* Hartree–Fock electronic energy can be obtained from the cross-sectional views, figures 3 (*b*) and (*c*). The baseline of the grid in these cross-cut views denotes the *exact* energy, and is observed to be almost superimposed on the $E_L{}^{HF}$ surface plane. For the Kołos–Roothaan wavefunction favourable cancellation of errors of opposite sign for $E_L{}^{HF}$ is expected to be less important compared to the Goodisman wavefunction.
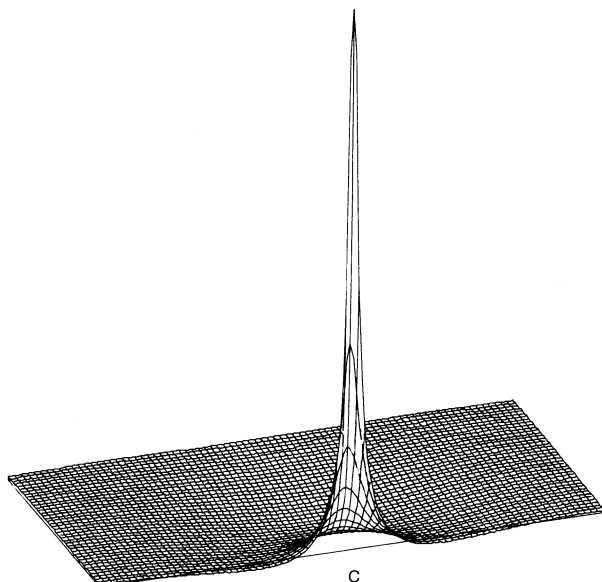

A

B

Figure 3. Reduced local energy error surface for H_2 using the nine-term Kołos–Roothaan Hartree–Fock wavefunction. The scales on the whole surface (a) and cross-sectional views ((b) and (c)) are the same as for figure 1.

4. DISCUSSION

There is a simple explanation for why the total electronic energy remain finite, despite the appearance of extremely large (infinite!) errors in the reduced local energy at the site of each nucleus. It can be shown (with some tedious algebra) that $E_L^{HF}(\xi, \eta)$ for the approximate wavefunctions [37–39] considered in this work blows up like

$$E_L^{HF}(\xi, \eta) \propto (\xi \pm \eta)^{-1} \qquad (7)$$

at each nucleus. Recall from equation (6) that $\xi \to 1$ and $\eta \to \pm 1$ at the hydrogen nuclei. When the total energy is evaluated from $E_L^{HF}(\xi, \eta)$, the required volume element factor (the angular term has already been taken into account in $E_L^{HF}(\xi, \eta)$) is

$$dV = \tfrac{1}{4} R \pi^3 (\xi^2 - \eta^2) \, d\xi \, d\eta. \qquad (8)$$

The critical factor in equation (8) is the term $(\xi^2 - \eta^2)$, which effectively wipes out the large errors present in the wavefunction in the region of each nucleus. There is no reason to expect that the evaluation of *all* expectation values, particularly those based on operators emphasizing the region very close to the nuclei, would exhibit exactly the same favourable reduction of errors in the wavefunction in the near nuclear region. Relevant discussion on the singular behaviour of the wavefunction applicable to the present study, can be found in the work of Kołos and Roothaan [39] and Pack and Byers-Brown [40].

The reduced local energy surface provides a very stringent probe of the *local* accuracy of the wavefunction, which in turn may be employed to predict the probable accuracy of various expectation values emphasizing different regions of

configuration space.   In the present study we have computed the reduced local energy for a very extensive number of configuration space coordinates.   For larger molecules, a simpler and less expensive approach would be the examination of the region in the immediate vicinity of each nucleus and each chemical bond. This approach would provide the key information necessary to examine the accuracy of the wavefunction in the region of principal chemical interest.

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