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## RESEARCH ARTICLE

## The Coulson-Fischer Wave Function: Parametrization using Distributed Gaussian Basis Sets

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A ‘generalized’ Coulson-Fischer wave function, in which the orbitals are approximated by means of a linear expansion in distributed Gaussian *s*-type basis functions, is used to determine a complete potential energy curve for the ground state of the hydrogen molecule by *ab initio* methods. A distributed basis set is developed in which both the positions and the exponents of Gaussian *s*-type functions are determined by invoking the variation principle. This basis set supports a sub- $\mu$ hartree level of accuracy and provides a reference with respect to which calculations, in which the exponents are generated using an even-tempered prescription and an anharmonic model, is employed to distribute the basis functions along the internuclear axis, can be assessed. This basis set also supports energy expectation values of a sub- $\mu$ hartree level of accuracy.

**Keywords:** Coulson Fischer theory, *ab initio* potential energy curves, distributed Gaussian basis sets, even-tempered basis sets, anharmonic distribution model

## 1. Introduction

Sixty years ago, in 1949, Coulson and Fischer published a paper[1] on the molecular orbital treatment of the ground state of the hydrogen molecule in which they presented a wave function providing a simple physical picture of the chemical bond, combining the advantages of molecular orbital and valence bond theory. In a recent publication[2], it has been emphasized that the Coulson-Fischer function is distinct from the molecular orbital and valence bond functions, and should be regarded as a ‘third way’ in quantum chemistry. Unlike the widely used Hartree-Fock molecular orbital wave function, the Coulson-Fischer wave function provides a qualitatively correct description of the molecular dissociation process, *i.e.*



It therefore provides a prototype for quantum chemical approximations which are applicable to complete potential energy curves and surfaces. Gerratt *et al.*[3] described the work of Coulson and Fischer as “a remarkably under-valued paper”.

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1 The Coulson-Fischer ansatz forms the precursor for a number of methods currently  
2 used in *ab initio* molecular electronic structure theory in studies where an entire  
3 potential energy curve is required. Examples include the ‘spin-coupled’ theory of  
4 Gerratt and Lipscomb[4, 5], the pair function model of Hurley *et al.*[6], the ‘gener-  
5 alised’ valence bond theory of Goddard and his coworkers[7, 8], and the ‘hierarchical  
6 tree’ methods proposed by one of us[2, 9].

7 The Coulson-Fischer wave function is built from a spatial function which can be  
8 written as a product of two non-orthogonal orbitals which are related by reflection  
9 in the plane perpendicular to the internuclear axis. Coulson and Fischer used a min-  
10 imum basis set consisting of a  $1s$  functions located on each of the component atoms.  
11 In 1975, Wilson and Gerratt[10] employed an extended basis set of exponential-type  
12 functions and demonstrated that their ‘generalized’ Coulson-Fischer wave function  
13 combines “conceptual simplicity” with “results of remarkable accuracy”. For ex-  
14 ample, the generalized Coulson-Fischer wave function recovers over 87.1% of the  
15 binding energy of the hydrogen molecule ground state.

16 The multireference character of a molecule typically changes across the poten-  
17 tial energy surface during bond formation or breaking. It is well known that the  
18 restricted Hartree-Fock (RHF) wave function includes unphysical terms at the dis-  
19 sociation limit undermining attempts to use single reference correlation methods,  
20 such as the popular CCSD(T) theory, in studies of chemical reactions. Furthermore,  
21 unrestricted Hartree-Fock (UHF) theory often results in qualitatively incorrect po-  
22 tential energy surfaces, particularly in the intermediate bond breaking region, be-  
23 cause of spin contamination[11–25] *i.e.* the mixing of unwanted spin states into the  
24 wave function, which results in unphysical barriers.

25 The continuing growth in the power of digital computing machines has facilitated  
26 increasingly accurate quantum chemical approximations. A fundamental approx-  
27 imation which is ubiquitous in molecular electronic structure calculations is the  
28 algebraic approximation[26] or expansions in a basis set of finite analytical func-  
29 tions - most often Gaussian-type functions. In recent work[27, 28], we have shown  
30 that distributed basis sets of  $s$ -type Gaussian functions can support the ground  
31 state Hartree-Fock energies for small diatomic molecules at the sub- $\mu$ Hartree level  
32 of accuracy. We have also demonstrated that a comparable level of accuracy can be  
33 achieved in four-component relativistic calculations for molecules using the Dirac-  
34 Hartree-Fock model[29]. In these basis sets, the exponents can be generated using  
35 the even-tempered prescription developed by Ruedenberg and his co-workers[30].  
36 It has been shown that an anharmonic model can be employed to distribute the  
37 basis functions. Distributed Gaussian basis sets defined in this way involve a single  
38 variational parameter for each geometry considered. The results can be compared  
39 with fully variation calculations in which both the exponents and positions of the  
40 basis functions are independently optimized. Further details can be found in our  
41 previous publications[27, 28].

42 The present work demonstrates the use of the distributed basis set approxi-  
43 mation, using the combination of the even-tempered prescription for generating  
44 exponents and the anharmonic model for defining the positions of the basis func-  
45 tions, for a wave function which is capable of supporting a qualitatively correct  
46 description of a complete potential energy curve from the united (He) atom to the  
47 separated H atoms. In the next section, we recall details of the Coulson-Fischer  
48 study which are relevant to the present work. Distributed basis sets are described  
49 in section 3, focussing on sets of  $s$ -type Gaussians with the exponents generated  
50 by assuming that they form a geometric progression and the distribution based  
51 on the anharmonic model. Section 4 contains both our results and discussion. Our  
52 conclusions are given in section 5.

## 2. The Coulson-Fischer Wave Function and Energy Expectation Value

In their seminal work, Coulson and Fischer[1] gave an explicit demonstration of the equivalence of the molecular orbital (MO) and valence bond (VB) models of molecular electronic structure when these approximations are sufficiently refined. Specifically, they showed that the VB function  $\psi = \{\psi_{cov} + k\psi_{ion}\}$ , with the covalent structure  $\psi_{cov} = \phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)$  and the ionic structure  $\psi_{ion} = \phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2)$  is equivalent to the two configuration MO function  $\psi = \{(\sigma_{1s})^2 - \mu(\sigma_{1s}^*)^2\}$ , where  $\sigma_{1s} = \phi_a + \phi_b$  is a bonding molecular orbital and  $\sigma_{1s}^* = \phi_a - \phi_b$  is an antibonding orbital. Furthermore, they showed that these VB and MO wave functions are equivalent to a third approximation  $\psi = (\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2))$  in which the orbitals have the form  $\varphi_a(1) = \phi_a(1) + \lambda\phi_b(1)$  and  $\varphi_b(2) = \phi_b(2) + \lambda\phi_a(2)$ . (In the above we have neglected the normalization factors in each approximate wave function.) In the Coulson-Fischer study, the orbitals  $\phi_a$  and  $\phi_b$  are  $1s$ -atomic orbitals centred on the two nuclei  $a$  and  $b$ . The third approximate wave function has been termed ‘different orbitals for different spins’ DODS or a ‘spin coupled wave function’. In recent work[2], we have emphasized that the Coulson-Fischer function is distinct from both the molecular orbital and the valence bond models. It represents a ‘third way’ in quantum chemistry.

The generalized Coulson-Fischer wave function of Wilson and Gerratt[10] has the form

$$\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2) = \sqrt{2}\mathcal{A}(\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)\Theta(\sigma_1, \sigma_2)) \quad (2)$$

where the spatial orbitals  $\varphi_1$  and  $\varphi_2$  are not orthogonal and are related by reflection in the plane perpendicular to the internuclear axis and passing through its midpoint, *i.e.*

$$\varphi_2 = \sigma_h\varphi_1, \quad (3)$$

and the two-electron spin function has the form

$$\Theta(\sigma_1, \sigma_2) = \sqrt{\frac{1}{2}}(\alpha_1\beta_2 - \beta_1\alpha_2), \quad (4)$$

where  $\alpha$  ( $\beta$ ) is the up (down) spin function.  $\mathcal{A}$  is the idempotent antisymmetrizer. When  $\varphi_1$  ( $\varphi_2$ ) is approximated by a  $1s$  atomic orbital centred on nucleus  $a$  ( $b$ ), the original Coulson-Fischer function is recovered.

In the ‘generalized’ Coulson-Fischer function, the orbitals are approximated by expansion in some arbitrary basis set  $\{\chi_p(\mathbf{r}) \equiv \langle \mathbf{r} | \chi_p \rangle, p = 1, 2, \dots, m\}$ , that is

$$|\varphi_i\rangle \simeq |\bar{\varphi}_i\rangle = \sum_{p=1}^m |\chi_p\rangle c_{ip}, \quad i = 1, 2. \quad (5)$$

In this equation, the coefficients  $c_{ip}$  determine the weight of each basis function in the approximation  $|\bar{\varphi}_i\rangle$  to the exact orbital  $|\varphi_i\rangle$ , where we have used the Dirac notation in which  $\bar{\varphi}_i \equiv \langle \mathbf{r} | \bar{\varphi}_i \rangle$  and  $\varphi_i \equiv \langle \mathbf{r} | \varphi_i \rangle$ . Equation (5) defines the algebraic approximation; the expansion in a set of finite analytical functions which is ubiquitous in practical computational quantum chemistry. It is assumed that as the size of the basis set  $m$  is increased, the approximation  $|\bar{\varphi}_i\rangle$  will converge the the exact

orbital  $|\varphi_i\rangle$ . (In the following discussion, we shall omit the bar when confusion will not arise.)

In their study, Wilson and Gerratt[10] employed an expansion in atom-centred exponential-type functions so that their approximations for the orbitals had the form

$$|\varphi_i\rangle = \sum_{p=1}^{m_a} |\chi_p^a\rangle c_{ip} + \sum_{p=1}^{m_b} |\chi_p^b\rangle c_{ip}, \quad i = 1, 2, \quad (6)$$

where the basis set  $\{|\chi_p^a\rangle, p = 1, 2, \dots, m_a\}$  is centred on nucleus  $a$  and the set  $\{|\chi_p^b\rangle, p = 1, 2, \dots, m_b\}$  is centred on nucleus  $b$ . (For a homonuclear system described by an atom-centred basis set, the exponents of the functions located on centre  $a$  are taken to be the same as those on centre  $b$ .) In more recent work, Moncrieff and Wilson[31] employed basis sets of atom-centred Gaussian-type functions as well as basis sets containing functions centred on the bond mid-point. In this case, the orbital approximations have the form

$$|\varphi_i\rangle = \sum_{p=1}^{m_a} |\chi_p^a\rangle c_{ip} + \sum_{p=1}^{m_c} |\chi_p^c\rangle c_{ip} + \sum_{p=1}^{m_b} |\chi_p^b\rangle c_{ip}, \quad i = 1, 2, \quad (7)$$

where the set  $\{|\chi_p^c\rangle, p = 1, 2, \dots, m_c\}$  is located at the bond centre. The exponents of the functions centred on the mid-point of the bond can be different from those centred on the two atomic nuclei. In this work, we employ distributed Gaussian basis sets which are defined in the next section, section 3.

The energy expectation value corresponding to the wave function (2) can be written

$$E = (1 + \langle\varphi_1|\varphi_2\rangle \langle\varphi_2|\varphi_1\rangle)^{-1} [\langle\varphi_1|h|\varphi_1\rangle + \langle\varphi_2|h|\varphi_2\rangle + \langle\varphi_1|\varphi_2\rangle \langle\varphi_2|h|\varphi_1\rangle + \langle\varphi_2|\varphi_1\rangle \langle\varphi_1|h|\varphi_2\rangle + \langle\varphi_1\varphi_2|g|\varphi_1\varphi_2\rangle + \langle\varphi_1\varphi_2|g|\varphi_2\varphi_1\rangle]. \quad (8)$$

where  $h$  is the one-electron component of the hamiltonian and  $g$  is the two-electron component.

For a given basis set, the orbitals can be determined by forming the Lagrangian

$$\mathcal{L} = E - \epsilon_1 \langle\varphi_1|\varphi_1\rangle - \epsilon_2 \langle\varphi_2|\varphi_2\rangle \quad (9)$$

and considering variations of the orbitals. This leads to the pseudo-eigenvalue equations

$$\mathcal{F}_1 |\varphi_1\rangle = \epsilon_1 |\varphi_1\rangle, \quad \langle\varphi_1|\varphi_1\rangle = 1 \quad (10)$$

and

$$\mathcal{F}_2 |\varphi_2\rangle = \epsilon_2 |\varphi_2\rangle, \quad \langle\varphi_2|\varphi_2\rangle = 1 \quad (11)$$

for the two orbitals. In practice, a self-consistent field process is employed to solve the orbital equations, solving first equation (10) then using equation (3) to improve the approximation for  $|\varphi_2\rangle$ . This process is repeated until self-consistency is achieved to within a certain accuracy.

The electronic energy depends not only on the orbital expansion coefficients,  $c_{ip}$ , but also on the basis set. Optimization of the parameters defining a given basis set

requires the gradient of the energy with respect to the exponents  $\zeta_p, p = 1, 2, \dots, m$  and positions of the basis functions  $\mathbf{r}_p, p = 1, 2, \dots, m$ . By defining the projection operator

$$\Pi = \sum_{p=1}^m |\chi_p\rangle \langle \chi_p| = \sum_{p=1}^m \sum_{q=1}^m |\chi_p\rangle \langle \chi_p | \chi_q\rangle \langle \chi_q|, \quad \text{where } \langle \chi_p | \chi_q\rangle = \langle \chi_p | \chi_q\rangle^{-1}, \quad (12)$$

the orbitals can be written as

$$|\varphi_i\rangle = \Pi |\varphi_i\rangle = \sum_{p=1}^m |\chi_p\rangle \langle \chi_p | \varphi_i\rangle = \sum_{p=1}^m |\chi_p\rangle c_{ip} \quad (13)$$

and variations  $|\delta\varphi_i\rangle$  take the form

$$|\delta\varphi_i\rangle = \Pi |\delta\varphi_i\rangle + \sum_{p=1}^m (\partial_{\mu_p} \Pi) |\delta\varphi_i\rangle \partial \mu_p \quad (14)$$

where

$$\partial_{\mu_p} \Pi = \frac{\partial \Pi}{\partial \mu_p}, \quad \mu_p = \{\zeta_p, \mathbf{r}_p\}. \quad (15)$$

The orbital equations can be cast in the form

$$\Pi (\mathcal{F}_i - \epsilon_i) \Pi |\varphi_i\rangle = 0, \quad i = 1, 2 \quad (16)$$

and the second term on the right-hand side of equation (14) leads to the equations for basis set optimization

$$\langle \varphi_i | (\partial_{\mu_p} \Pi) \mathcal{F}_i | \varphi_i\rangle = 0, \quad \mu_p = 1, 2, \dots, M \quad (17)$$

In the present case  $M = 2m$  since there is an exponent and one position of the corresponding Gaussian function to optimize for each function in the distributed basis set for the ground state of the  $\text{H}_2$  molecule. The derivative of the projection operator  $\Pi$  with respect to the basis set parameters can be written as

$$\partial_{\mu_p} \Pi = (I - \Pi) |\partial_{\mu_p} \chi_p\rangle \langle \chi_p| + |\chi_p\rangle \langle \partial_{\mu_p} \chi_p| (I - \Pi). \quad (18)$$

Substituting equation (18) into (17) gives the expression

$$\langle \varphi_i | \chi_p\rangle \langle \partial_{\mu_p} \chi_p | (I - \Pi) \mathcal{F}_i | \varphi_i\rangle = c_{ip} \langle \partial_{\mu_p} \chi_p | (I - \Pi) \mathcal{F}_i | \varphi_i\rangle = 0. \quad (19)$$

By taking account of equation (16), we are led to the relation

$$c_{ip} \langle \partial_{\mu_p} \chi_p | (\mathcal{F}_i - \epsilon_i) | \varphi_i\rangle = 0 \quad (20)$$

the left-hand side being the gradient of the energy with respect to the basis set parameters  $\zeta_p$  and  $\mathbf{r}_p$ .

$$\frac{\partial E}{\partial \mu_p} = c_{ip} \langle \partial_{\mu_p} \chi_p | (\mathcal{F}_i - \epsilon_i) | \varphi_i\rangle \quad (21)$$

In this present study, a direct optimization procedure was used to determine the variational parameters defining the basis sets in which derivatives were not explicitly evaluated[32, 33].

### 3. Distributed Gaussian Basis Sets

In distributed Gaussian basis sets of  $s$ -type functions, the exponents and the distribution of the Gaussian basis functions are generated according to empirical prescriptions which are constructed so as to ensure that the set becomes complete in the limit  $m \rightarrow \infty$ . The distributed Gaussian basis set approach should be distinguished from the use Gaussian lobe functions [34–38] and from the floating spherical Gaussian orbital (FSGO) model [39–43] in that there is no attempt to mimic higher harmonics directly, and nonlinear optimization is avoided. This allows the use of large basis sets, resulting in high precision.

The approximate orbitals are written

$$\varphi_i(\mathbf{r}) = \sum_{p=1}^m \chi_p(\zeta_p, \mathbf{r}_p; \mathbf{r}) c_{ip} \quad \text{or} \quad |\varphi_i\rangle = \sum_{p=1}^m |\chi_p\rangle c_{ip} \quad (22)$$

where the  $c_{ip}$  are orbital expansion coefficients and the  $s$ -type Gaussian basis functions are defined as follows

$$\chi_p(\zeta_p, \mathbf{r}_p; \mathbf{r}) = \left(\frac{2\zeta_p}{\pi}\right)^{\frac{3}{4}} \exp\left(-\zeta_p |\mathbf{r} - \mathbf{r}_p|^2\right). \quad (23)$$

In this expression,  $\zeta_i$  is the exponent and  $\mathbf{r}_p = (x_p, y_p, z_p)$  is the position of the function.

The parameters defining the basis sets,  $\zeta_p$  and  $\mathbf{r}_p$ , can be determined by invoking the variation principle[44–47]. However, it has been established that the even-tempered prescription in which the exponents are taken to form a geometric sequence

$$\zeta_p = \alpha\beta^p, p = 1, 2, \dots, m \quad (24)$$

can be very useful[27, 28].  $\alpha$  and  $\beta$  can be taken to be functions of  $m$ . In 1979, it was established[30] that for atoms well-defined schemes can be constructed such that even-tempered basis sets approach a complete set in the limit of large  $m$  and, therefore, the HartreeFock limit is approached.

In more recent work[27, 28], it has been shown that an anharmonic model can be profitably used to distribute the basis functions along the internuclear axis in diatomic molecules, **which is taken to coincide with the  $x$ -axis**. We used a series of anharmonic distributions with shifted origins to generate subsets of functions centred on regularly spaced points lying on the straight line passing through the two nuclei. The first subset of anharmonically distributed functions is generated according to the formula

$$x_p = X_N + \Delta x_{p+}, \quad p = 1, 2, \dots, m_1 \quad (25)$$

where  $X_N$  is the coordinate of a nucleus and  $m_1$  is the number of functions in the

1 first even-tempered subset. The shifts,  $\Delta x_p$ , are given by

$$2 \Delta x_{p\pm} = \frac{1}{k} \left[ -\zeta_p^2 \pm \sqrt{\zeta_p^4 + \frac{kZ}{2R^2}} \right] \quad (26)$$

3 where the subscript  $\pm$  on the left-hand side distinguishes between the two roots  
4 on the right-hand side,  $Z$  is a nucleus charge and  $R$  an internuclear distance. The  
5 parameter  $k$  is determined by invoking the variation theorem. The functions in the  
6 second subset are distributed according to the relation

$$7 x_q = X_N + \Delta x_0 + \Delta x_{q+}, \quad q = 1, 2, \dots, m_2 \quad (27)$$

8 where  $m_2$  ( $< m_1$ ) is the number of functions in the second subset and  $\Delta x_0$  is  
9 related to  $k$  through the equation[27, 28]

$$10 \Delta x_0 = \frac{1}{R} \sqrt{\frac{Z}{2k}}. \quad (28)$$

11 The exponents are taken from the lower elements in the even-tempered sequence  
12 (24). For the third subset, the positions of the functions are defined by

$$13 x_r = X_N + 2\Delta x_0 + \Delta x_{r+}, \quad r = 1, 2, \dots, m_3 \quad (29)$$

14  $m_3 < m_2$ . This series of anharmonic distributions with shifted origins lying between  
15 the two nuclei is supplemented by subsets of functions centred on the line passing  
16 through the nuclei but beyond the internuclear region. These functions centred on  
17 the points

$$18 x_t = X_N - (n-1)\Delta x_0 + \Delta x_{t-}, \quad t = 1, 2, \dots, m_{[-n]} \quad (30)$$

19 are able to describe the depletion of charge beyond the nuclei. The anharmonic  
20 scheme allows the use of a single variational parameter for different nuclei.

21 We use the following notation to describe a distributed basis set defined by a  
22 series of subsets each constructed using an anharmonic model:

$$23 ([m_1 + m_2 + \dots]) ([m_{-1} + \dots])_X. \quad (31)$$

24 In this notation,  $X$  is the nucleus with respect to which the basis set is defined,  
25 the first [...] defines the subsets of functions lying on the internuclear axis and the  
26 second [...] the subsets located beyond the internuclear region.  $m_{-1}, \dots$  denotes  
27 the number of functions in each of this second set of basis subsets.

#### 28 4. Results and Discussion

29 In a recent publication[28], we have shown that a distributed Gaussian basis set of  
30  $s$ -type functions generated by the even-tempered/anharmonic model prescription  
31 can support a HartreeFock ground-state energy of the  $H_2$  molecule of  $-1.133\ 629\ 16$   
32 hartree at the experimental equilibrium geometry of  $1.400$  bohr. A finite difference  
33 HartreeFock calculation[28] performed at the same geometry using a grid desig-  
34 nated  $[259 \times 565; 150]$  gave a ground-state energy of  $-1.133\ 629\ 571\ 47$  hartree.  
35 The basis set truncation error in the finite basis set calculation is therefore  $\sim 0.41$

1  $\mu$  hartree. In earlier calculations[45], it had been shown that a ground state ma-  
2 trix Hartree-Fock energy of  $-1.133\ 629\ 523\ 3$  hartree can be supported by a  
3 distributed basis set of  $s$ -type Gaussians in which both the exponents and the  
4 basis functions' positions were variationally optimized. The fully optimized matrix  
5 Hartree-Fock energy lies  $\sim 0.36\ \mu$ hartree below that associated with the even-  
6 tempered/anharmonic model prescription.  
7

8 In the present study, the use of a distributed basis set of  $s$ -type Gaussian func-  
9 tions generated by the even-tempered prescription and an anharmonic model in  
10 a Coulson-Fischer calculation for the experimental equilibrium geometry gave a  
11 ground state energy of  $-1.152\ 159\ 43$  hartree,  $0.018\ 529\ 858\ 53$  hartree below the  
12 corresponding finite difference Hartree-Fock value. Fully optimizing the exponents  
13 and positions of the basis functions gave a Coulson-Fischer energy of  $-1.152\ 159\ 81$   
14 hartree. The difference between these two matrix Coulson-Fischer energies is  $\sim 0.38$   
15 which is comparable with the corresponding difference measured for the matrix  
16 Hartree-Fock energies and suggests that the results are close to the basis set limit  
17 to a sub- $\mu$ hartree level.  
18

19 In Table 1, the results of previously published calculations for the  $H_2$  ground  
20 state employing the Coulson-Fischer wave function are compared with the present  
21 calculations for the experimental equilibrium geometry. All of these calculations  
22 used expansions in finite analytical functions to parametrize the Coulson-Fischer  
23 orbitals. The calculations may therefore be described as an application of the *ma-*  
24 *trix* Coulson-Fischer method. The original study by Coulson and Fischer used a  
25 minimum basis set. The matrix Coulson-Fischer calculations summarized in Table  
26 1 employed extended basis sets. To our knowledge, there are no published finite  
27 difference or finite element electronic structure calculations for the Coulson-Fischer  
28 wave function.  
29

30 In the second part of Table 1, we have collected the results of Hartree-Fock  
31 calculations for the  $H_2$  ground state at the experimental equilibrium geometry,  
32 which are relevant to the present discussion. For the Hartree-Fock model both  
33 finite difference and finite element calculations have been reported in addition to a  
34 number of finite basis set calculations which support an accuracy approaching that  
35 given by the fully numerical studies. These calculations provide valuable measures  
36 of basis set truncation errors.  
37

38 Table 1 also records the total energies obtained in four-component Dirac-Hartree-  
39 Fock and Dirac-Hartree-Fock-Breit calculations. Both finite basis set and finite ele-  
40 ment calculations have been reported for the Dirac-Hartree-Fock model. All of the  
41 finite basis set Dirac-Hartree-Fock calculations collected in Table 1 employed the  
42 relativistic algebraic approximation in the 'strict kinetic balance' form, *i.e.* there  
43 is a one-to-one correspondence between the large and small component basis func-  
44 tions used to parametrize the four-component spinors. Parpia and Mohanty[55] em-  
45 ployed the finite basis set of Gaussian function developed by Wells and Wilson[54]  
46 to approximate the large component of the molecular spinor and the 'strict kinetic  
47 balance' condition to generate their small component basis set. Quiney *et al*[29]  
48 employed a distributed basis set of  $s$ -type Gaussian functions, the large component  
49 basis set being constructed from that developed by Glushkov and Wilson[45] in a  
50 nonrelativistic calculations in which both the exponents and the basis function  
51 positions were fully optimized by invoking the variation principle. The small com-  
52 ponent basis set was again obtained by using the 'strict kinetic balance' condition.  
53 For the Dirac-Hartree-Fock-Breit model, in which the electron-electron interaction  
54 is described by the sum of a Coulomb term and the frequency-independent Breit  
55 operator, only the finite basis set calculations of Quiney *et al*[29] have been re-  
56 ported. These calculations also employed a distributed basis set of  $s$ -type Gaussian  
57  
58  
59  
60

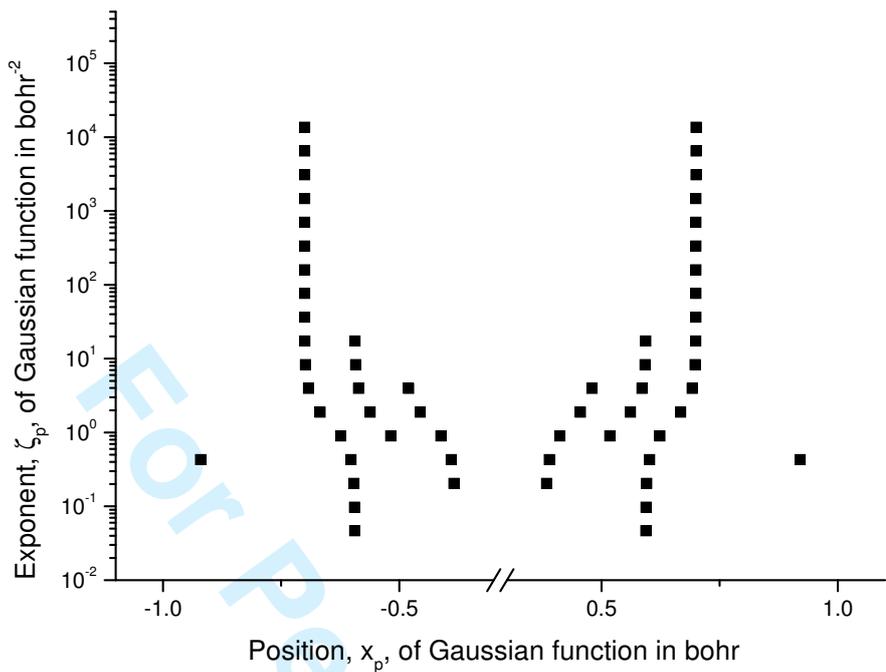


Figure 1. Distributed Gaussian basis set for the ground state of the H<sub>2</sub> molecule at the equilibrium nuclear geometry with even-tempered exponents and basis function positions determined by an anharmonic model. The nuclei are located at 0.7 bohr.

functions derived from the nonrelativistic calculations reported by Glushkov and Wilson[45]. All of the calculations reported in Table 1 employed a point charge model for the nuclei.

The exponents and basis function positions obtained by using the even-tempered **recipe** to generate the exponents and the anharmonic model to determined the positions are displayed in Figure 1. The nuclei are separated by 1.400 bohr and located at  $\pm 0.7$  bohr. The basis subset associated with each of the nuclei has the form  $[18 + 5 + 5][0 + 1]_{\text{H}}$ . The exponents and basis function positions are tabulated in the supplementary material. These parameters were used to generate an initial guess for a fully variational calculation. In Figure 2, the fully optimized exponents and basis function positions for a distributed Gaussian basis set of 58 *s*-type Gaussian functions are displayed. Again, the nuclei are separated by 1.400 bohr and located at  $\pm 0.7$  bohr. The basis subset associated with each of the nuclei has the form  $[18 + 5 + 5][0 + 1]_{\text{H}}$  and is given in the supplementary material for this paper.

Two numerical potential energy curves for the Coulson-Fischer wave function are shown in Table 2. In this table, *R* is the nuclear separation. Values of *R* from 0.90 bohr to 10.00 bohr are considered. The first column of energies, which is headed  $E_{\text{CF}}^{(ET/AM)}$ , gives values of the Coulson-Fischer energy, in hartree, supported by a distributed Gaussian basis set of *s*-type functions with exponents determined by the even-tempered prescription and basis function positions given by the anharmonic model. The second column, headed  $E_{\text{CF}}^{\text{opt.}}$ , gives the energies obtained by fully optimizing both the exponents and the positions of the basis functions. The values of  $E_{\text{CF}}^{\text{opt.}}$  lie below those of  $E_{\text{CF}}^{(ET/AM)}$ . The differences between these energies are given in  $\mu$ hartree in the final column of Table 2.

Table 1. Comparison of the total electronic energies given by the Coulson-Fischer, Hartree-Fock and Dirac-Fock wave functions at  $R = 1.4$  bohr for the ground state energies of the hydrogen molecule.

Method	Details	Author(s)	$E^a$	Reference
Coulson-Fischer	atom-centred basis set of exponential-type functions	Wilson and Gerratt	-1.151 751	[10]
	atom-centred basis set of Slater functions	Wilson and Goddard	-1.151 887	[48]
	atom-centred basis set of Gaussian-type functions	Moncrieff and Wilson	-1.152 159 27	[31]
	atom- and bond-centred basis set of Gaussian-type functions	Moncrieff and Wilson	-1.152 159 31	[31]
	distributed basis set of $s$ -type Gaussian functions generated by the even-tempered prescription and an anharmonic model	Glushkov and Wilson	-1.152 159 45	present work
	fully optimized distributed basis set of $s$ -type Gaussian functions	Glushkov and Wilson	-1.152 159 81	present work
	finite difference	Kolos and Roothaan	-1.133 630	[49]
	finite difference	Laaksonen, Pyykkö and Sundholm	-1.133 629 57	[50]
	finite difference	Kobus quoted by Jensen	-1.133 629 571 5	[51, 52]
	finite element	Glushkov, Kobus and Wilson	-1.133 629 571 47	[28]
Hartree-Fock	basis set of elliptical functions	Yang, Heinemann and Kolb	-1.133 629 571 7(2)	[53]
	finite basis set of Gaussian-type functions	Wells and Wilson	-1.133 629 57	[54]
	finite basis set of Gaussian-type functions	Wells and Wilson	-1.133 629 44	[54]
	finite basis set of Gaussian-type functions	Moncrieff and Wilson	-1.133 628 90	[31]
	fully optimized distributed basis set of $s$ -type Gaussian functions	Glushkov and Wilson	-1.133 629 52	[45]
	finite basis set of Gaussian-type functions in an LCAO approximation	Mitin	-1.133 629 571 456	[57]
	finite basis set of Gaussian-type functions	Parpia and Mohanty	-1.133 643 833 4	[55]
	finite element	Yang, Heinemann and Kolb	-1.133 643 970 08(1)	[53]
	finite element	Kullie, Dusterhöft and Kolb	-1.133 643 970 5	[56]
	distributed basis set of $s$ -Gaussian-type functions	Quiney, Glushkov and Wilson	-1.133 643 868 8	[29]
Dirac-Hartree-Fock	distributed basis set of $s$ -Gaussian-type functions	Quiney, Glushkov and Wilson	-1.133 629 410 6	[29]

<sup>a</sup>Total electronic energies are in hartree.

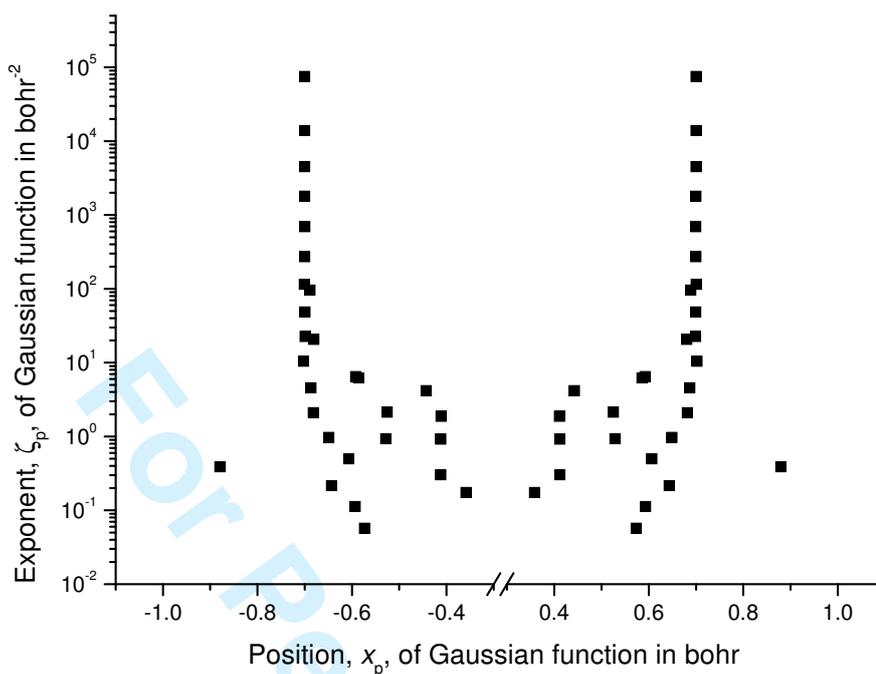


Figure 2. Distributed Gaussian basis set for the ground state of the  $H_2$  molecule at the equilibrium nuclear geometry with fully optimized exponents and basis function positions. The nuclei are located at  $\pm 0.7$  bohr.

Table 2. Total electronic energies given by the Coulson-Fischer wave function as a function of internuclear distance,  $R$ . The Coulson-Fischer energy,  $E_{CF}$ , is calculated for a distributed basis set of  $s$ -type functions in which the distribution is determined (i) from an even-tempered prescription for the exponents and an anharmonic model for the basis function positions ( $E_{CF}^{(ET/AM)}$ ) and (ii) by a full optimization of the basis function exponents and positions ( $E_{CF}^{opt.}$ ).

$R$	distributed basis set	$E_{CF}^{(ET/AM)}$	$E_{CF}^{opt.}$	$\Delta E_{CF}^{(ET/AM);opt.}$
0.90	[18+5+5][0]H	-1.056 734 49	-1.056 735 09	0.61
1.00	[18+5+5][0]H	-1.098 585 64	-1.098 586 09	0.45
1.10	[18+5+5][0]H	-1.125 037 37	-1.125 037 73	0.37
1.20	[18+5+5][0]H	-1.140 831 18	-1.140 831 51	0.34
1.30	[18+5+5][0+1]H	-1.149 143 51	-1.149 143 83	0.32
1.35	[18+5+5][0+1]H	-1.151 205 26	-1.151 205 56	0.30
1.40	[18+5+5][0+1]H	-1.152 159 45	-1.152 159 81	0.38
1.45	[18+5+5][0+1]H	-1.152 180 37	-1.152 180 71	0.34
1.50	[18+5+5][0+1]H	-1.151 415 53	-1.151 415 87	0.34
1.60	[18+5+5][0+1]H	-1.148 011 94	-1.148 012 28	0.34
1.70	[18+5+5][0+1]H	-1.142 748 63	-1.142 748 94	0.31
1.80	[18+5+5][0+1]H	-1.136 214 69	-1.136 214 96	0.27
2.00	[18+5+5][0+1]H	-1.120 979 16	-1.120 979 41	0.25
2.50	[18+5+5][0+1]H	-1.080 971 90	-1.080 972 33	0.43
3.00	[18+5+5][0+1]H	-1.048 316 30	-1.048 317 01	0.71
3.50	[18+5+5][0+1]H	-1.026 197 69	-1.026 198 61	0.92
4.00	[18+5+5][0+1]H	-1.013 143 11	-1.013 143 85	0.74
5.00	[18+5+5][0+1]H	-1.002 846 52	-1.002 846 82	0.30
6.00	[18+5+5][0+1]H	-1.000 555 27	-1.000 555 49	0.22
7.00	[18+5+5][0+1]H	-1.000 102 35	-1.000 102 49	0.14
8.00	[20+6+3][0]H	-1.000 018 08	-1.000 018 29	0.21
10.00	[20+6+3][0]H	-1.000 000 31	-1.000 000 53	0.22

<sup>a</sup>Total electronic energies are in hartree; energy differences are in  $\mu$ hartree; internuclear distances are in bohr.

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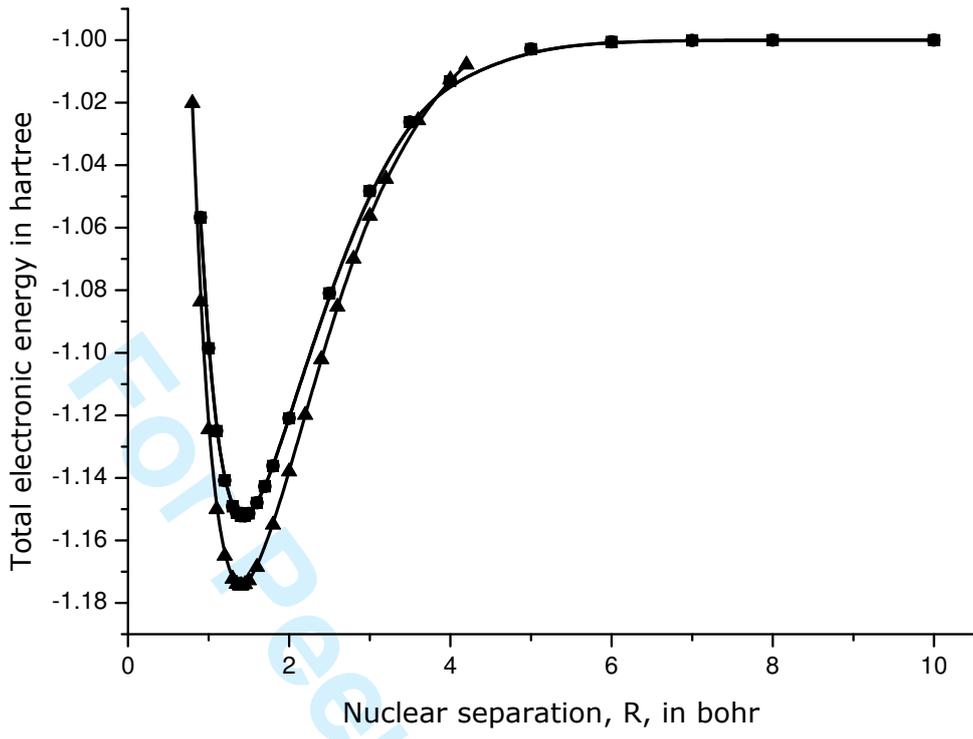


Figure 3. Potential energy curves for the ground state of the hydrogen molecule. The calculated points on the curves are labelled as follows:- ■: energy corresponding to the Coulson-Fischer wave function using a distributed Gaussian basis set with even-tempered exponents and basis function positions determined by an anharmonic model; ●: energy corresponding to the Coulson-Fischer wave function using a distributed Gaussian basis set with fully optimized exponents and basis function positions; ▲: energy corresponding to the extended James-Coolidge wavefunction. On the scale employed in this Figure, the points ■ and ● are coincident.

The two potential energy curves tabulated in Table 2 are plotted in Figure 3 using splines to interpolate the numerical values. The Coulson-Fischer potential energy curves are compared with the curve obtained in the extended James-Coolidge calculations of Kofos and Rootaahn[49]. Note that the Coulson-Fischer curve lies below that reported by Kofos and Rootaahn for values of  $R$  greater than  $\sim 4$  bohr.

Values of  $E_{CF}^{opt.}$  and  $E_{CF}^{(ET/AM)}$  were calculated for nuclear separations close to the equilibrium value. The corresponding Hartree-Fock energies were also calculated. The numerical potential energy curves for internuclear distances close to equilibrium are given in the supplementary material. The curves are plotted in Figure 4 using splines to interpolate between the calculated values.

Whereas the Hartree-Fock model under estimates the equilibrium nuclear separation, the Coulson-Fischer wave function yields an overestimation. This is in agreement with the previous work of Wilson and Gerratt[10] who reported a value of  $R_e$  of 1.427 bohr. The Coulson-Fischer function includes longitudinal correlation effects. Adding a second function which describes in-out or radial correlation, Wilson and Gerratt[10] found that  $R_e$  was reduced to 1.412 bohr. Adding a function describing angular correlation led to an  $R_e$  value of 1.418 bohr[10]. (Herzberg[58] gives an experimental value of  $R_e$  of 1.4006 bohr.)

In Figure 5, the ‘shift’ parameter  $\Delta x_0$  determining the anharmonic distribution model is plotted against internuclear separation. The numerical values are given in

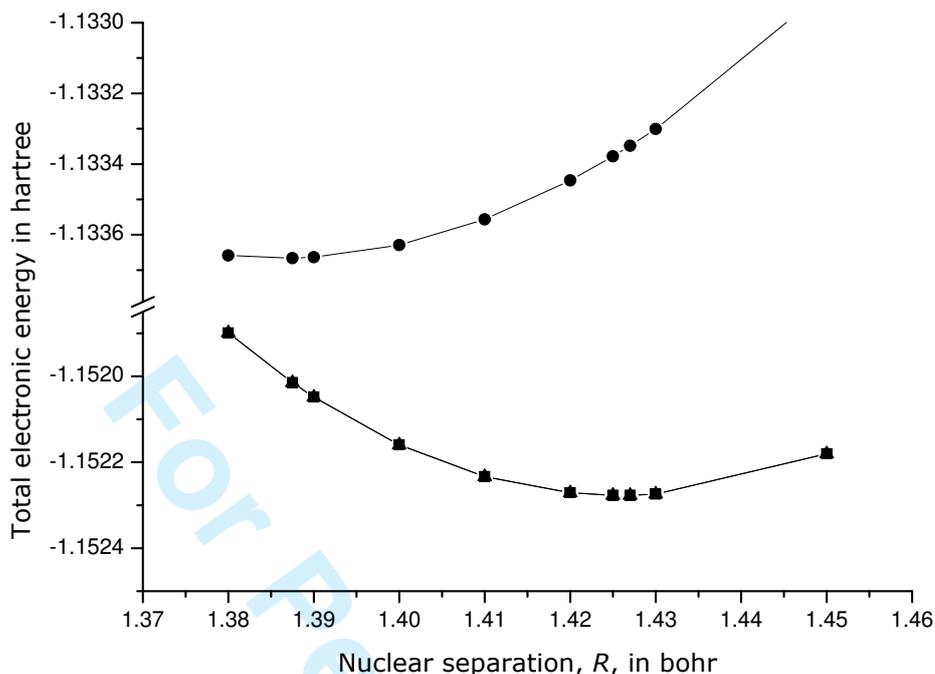


Figure 4. Potential energy curves for the ground state of the hydrogen molecule for nuclear separations close to the equilibrium value. The calculated points on the curves are labelled as follows:- ■: energy corresponding to the Coulson-Fischer wave function using a distributed Gaussian basis set with even-tempered exponents and basis function positions determined by an anharmonic model; ●: energy corresponding to the Hartree-Fock wave function using a distributed Gaussian basis set with even-tempered exponents and basis function positions determined by an anharmonic model.

the supplementary material to this paper.

## 5. Conclusions

The Coulson-Fischer wave function combines “conceptual simplicity” with “results of remarkable accuracy”. In this paper, we have shown that, unlike the widely used Hartree-Fock function, the Coulson-Fischer function can yield an *ab initio* description of the entire potential energy curve and that, when implemented with a distributed basis set of *s*-type Gaussian functions, the energy of the Coulson-Fischer model can be determined to a sub- $\mu$ hartree level.

When *ab initio* molecular electronic structure theory is used to determine entire potential energy curves, the Coulson-Fischer ansatz forms the precursor for a number of methods in current use. A recent short review has been given by one of us[2]. ‘Hierarchical tree’ methods[2, 9] show particular promise. The present study demonstrates that an efficient approach to complete basis set limit for methods based on the Coulson-Fischer approach is afforded by distributed basis sets of *s*-type Gaussian functions in which an even-tempered prescription for generating the exponents is employed in conjunction with the anharmonic model for distributing the basis functions.

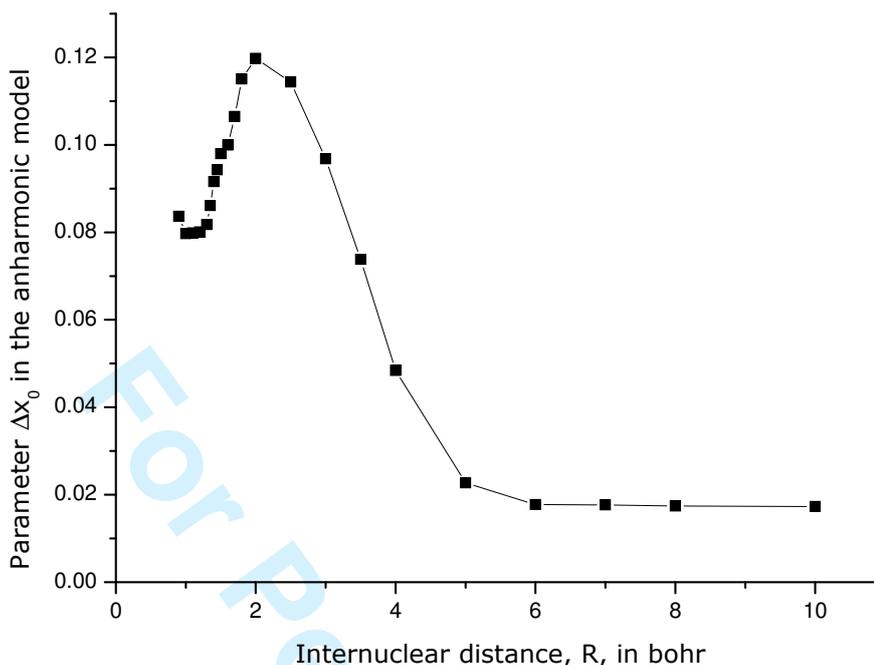


Figure 5. Plot of the 'shift' parameter  $\Delta x_0$  determining the anharmonic distribution model against internuclear separation.

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**SUPPLEMENTARY DATA TO RESEARCH ARTICLE**

**The Coulson-Fischer Wave Function: Parametrization using Distributed Gaussian Basis Sets**

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(15 August 2009)

**1. Introduction**

This supplement provides additional data for our paper *The Coulson-Fischer Wave Function: Parametrization using Distributed Gaussian Basis Sets* published in *Molecular Physics*[1].

**2. Supplementary tables**

In Table 1, the total electronic energies given by the Coulson-Fischer wave function for internuclear distance,  $R$  close to the equilibrium value. The Coulson-Fischer energy,  $E_{CF}$ , is calculated for a distributed basis set of  $s$ -type functions in which the distribution is determined:

- (i) from an anharmonic model ( $E_{CF}^{DBS(ET/AM)}$ ) and
- (ii) by a full optimization of the basis function exponents and positions ( $E_{CF}^{Opt.}$ ).

The Hartree-Fock energies supported by a distributed basis set are also given.

In Table 2, the distributed Gaussian basis set of  $s$ -type functions for the Coulson-Fischer ground state of the  $H_2$  molecule with a nuclear separation of 1.4 bohr with even-tempered exponents and basis function positions determined by an anharmonic model. Exponents,  $\zeta_p$ , are given in bohr<sup>-2</sup>. Basis function positions,  $x_p$ , are given in bohr. The nuclei are located at  $\pm 0.7$  bohr. The parameters for basis functions closer to one nucleus are given. The parameters for the basis functions closer to the other nucleus are related to those given by symmetry.

In Table 3, the distributed Gaussian basis set of  $s$ -type functions for the Coulson-Fischer ground state of the  $H_2$  molecule with a nuclear separation of 1.4 bohr with fully optimized exponents and basis function positions. Exponents,  $\zeta_p$ , are given in bohr<sup>-2</sup>. Basis function positions,  $x_p$ , are given in bohr. The nuclei are located at  $\pm 0.7$  bohr. The parameters for basis functions closer to one nucleus are given. The

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Table 1. Total electronic energies given by the Coulson-Fischer wave function for internuclear distance,  $R$  close to the equilibrium value. The Coulson-Fischer energy,  $E_{CF}$ , is calculated for a distributed basis set of  $s$ -type functions in which the distribution is determined (i) from an anharmonic model ( $E_{CF}^{DBS(ET/AM)}$ ) and (ii) by a full optimization of the basis function exponents and positions ( $E_{CF}^{opt.}$ ). The Hartree-Fock energies supported by a distributed basis set are also given.

$R$	$E_{CF}^{DBS(ET/AM)}$	$E_{CF}^{opt.}$	$E_{HF}^{DBS(ET/AM)}$
1.38	-1.151 898 87	-1.151 899 18	-1.133 658 68
1.3875	-1.152 014 71	-1.152 015 05	-1.133 666 18
1.39	-1.152 048 43	-1.152 048 78	-1.133 663 67
1.40	-1.152 159 43	-1.152 159 81	-1.133 629 05
1.41	-1.152 233 20	-1.152 233 54	-1.133 556 27
1.42	-1.152 270 99	-1.152 271 30	-1.133 446 42
1.425	-1.152 276 76	-1.152 277 10	-1.133 377 99
1.427	-1.152 276 67	-1.152 277 02	-1.133 348 15
1.43	-1.152 273 99	-1.152 274 32	-1.133 300 76
1.45	-1.152 180 37	-1.152 180 71	-1.132 906 65
Basis set	[18+5+5] [0+1] 58s	58s	[18+7+3] [0+1] 58s

<sup>a</sup>Total electronic energies are in hartree; internuclear distances are in bohr.

Table 2. Distributed Gaussian basis set of  $s$ -type functions for the Coulson-Fischer ground state of the  $H_2$  molecule with a nuclear separation of 1.4 bohr with even-tempered exponents and basis function positions determined by an anharmonic model. Exponents,  $\zeta_p$ , are given in bohr<sup>-2</sup>. Basis function positions,  $x_p$ , are given in bohr. The nuclei are located at  $\pm 0.7$  bohr. The parameters for basis functions closer to one nucleus are given. The parameters for the basis functions closer to the other nucleus are related to those given by symmetry.

$p$	$x_p$	$\zeta_p$
1	0.5941302	0.04647703
2	0.5944523	0.09744001
3	0.5958562	0.2042849
4	0.6018019	0.4282872
5	0.6237383	0.8979125
6	0.6674113	1.882491
7	0.6918595	3.946679
8	0.6981375	8.27429
9	0.6995761	17.34721
10	0.6999036	36.36877
11	0.6999781	76.24783
12	0.699995	159.8551
13	0.6999989	335.1393
14	0.6999997	702.626
15	0.6999999	1473.069
16	0.7	3088.318
17	0.7	6474.719
18	0.7	13574.37
19	0.5177735	0.8979125
20	0.5614465	1.882491
21	0.5858947	3.946679
22	0.5921727	8.27429
23	0.5936113	17.34721
24	0.3839266	0.2042849
25	0.3898723	0.4282872
26	0.4118087	0.8979125
27	0.4554817	1.882491
28	0.4799299	3.946679
29	0.9203106	0.4282872

Table 3. Distributed Gaussian basis set of  $s$ -type functions for the Coulson-Fischer ground state of the  $H_2$  molecule with a nuclear separation of 1.4 bohr with fully optimized exponents and basis function positions. Exponents,  $\zeta_p$ , are given in bohr<sup>-2</sup>. Basis function positions,  $x_p$ , are given in bohr. The nuclei are located at  $\pm 0.7$  bohr. The parameters for basis functions closer to one nucleus are given. The parameters for the basis functions closer to the other nucleus are related to those given by symmetry.

$p$	$x_p$	$\zeta_p$
1	0.57342	0.0570336
2	0.5932165	0.1122765
3	0.6431743	0.2156411
4	0.6066321	0.4971679
5	0.6490924	0.9695312
6	0.6817344	2.099289
7	0.6867978	4.556315
8	0.7023354	10.43203
9	0.699092	22.59744
10	0.699437	48.59312
11	0.6888008	96.22305
12	0.7005796	114.6467
13	0.6999989	272.1116
14	0.699533	694.4621
15	0.6999999	1795.93
16	0.7	4502.506
17	0.7	13876.37
18	0.7	75097.13
19	0.5285939	0.9343055
20	0.5253385	2.13261
21	0.5858937	6.228144
22	0.5921727	6.465771
23	0.6806014	20.57633
24	0.3584695	0.1745691
25	0.4119262	0.30335
26	0.4120533	0.9179386
27	0.4112176	1.871985
28	0.4428913	4.178819
29	0.8793649	0.3873786

parameters for the basis functions closer to the other nucleus are related to those given by symmetry.

In Table 4, values of the ‘shift’ parameter  $\Delta x_0$  are given as a function of internuclear distance  $R$ .

### 3. Supplementary Figures

In Figure 1, the distributed Gaussian basis set for the ground state of the  $H_2$  molecule for an internuclear distance,  $R$ , of 4.0 bohr is shown for even-tempered exponents and basis function positions determined by an anharmonic model. The nuclei are located at  $\pm 0.7$  bohr.

In Figure 2, the distributed Gaussian basis set for the ground state of the  $H_2$  molecule for an internuclear distance,  $R$ , of 4.0 bohr is shown for fully optimized exponents and basis function positions. Again, the nuclei are located at  $\pm 0.7$  bohr.

### References

[1] V.N. Glushkov and S. Wilson, *Molecular Physics (submitted for publication)*

Table 4. Values of the 'shift' parameter  $\Delta x_0$  as a function of internuclear distance  $R$ .<sup>a</sup>

$R$	$\Delta x_0$
0.9	8.368000(-2)
1	7.968000(-2)
1.1	7.988200(-2)
1.2	8.010400(-2)
1.3	8.176856(-2)
1.35	8.610158(-2)
1.4	9.159648(-2)
1.45	9.430276(-2)
1.5	9.798409(-2)
1.6	9.995437(-2)
1.7	1.064898(-1)
1.8	1.150754(-1)
2	1.197932(-1)
2.5	1.143678(-1)
3	9.680713(-2)
3.5	7.380835(-2)
4	4.839946(-2)
5	2.271912(-2)
6	1.773746(-2)
7	1.766658(-2)
8	1.741642(-2)
10	1.732141(-2)

<sup>a</sup>Powers of ten are given in parentheses.

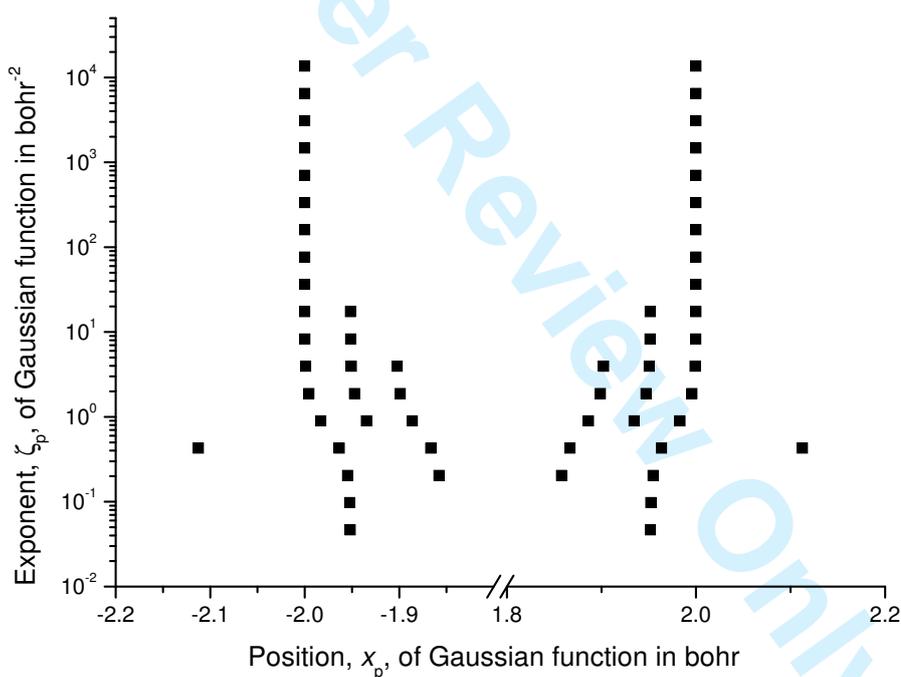


Figure 1. Distributed Gaussian basis set for the ground state of the  $H_2$  molecule for an internuclear distance,  $R$ , of 4.0 bohr with even-tempered exponents and basis function positions determined by an anharmonic model. The nuclei are located at 0.7 bohr.

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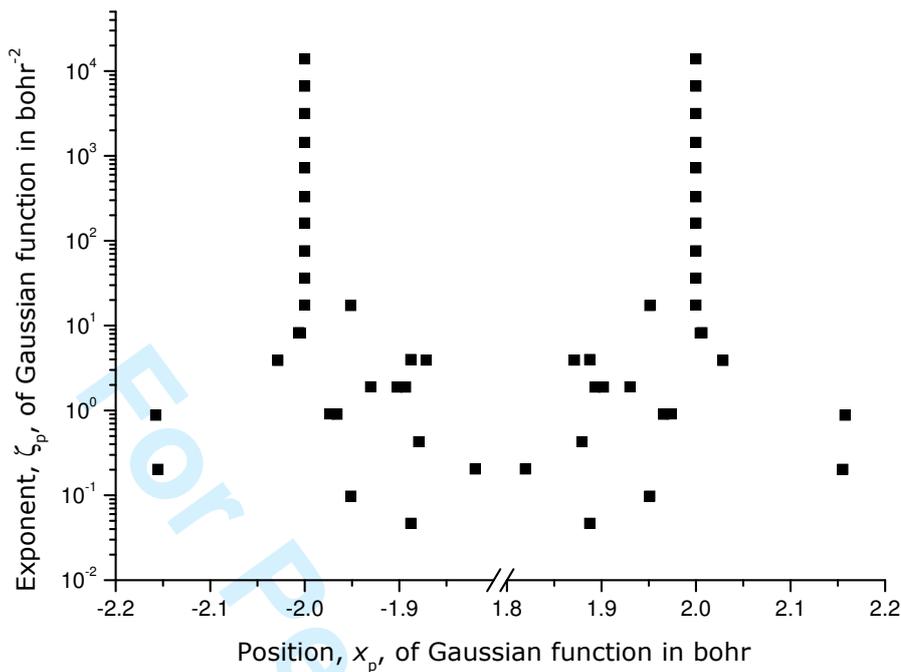
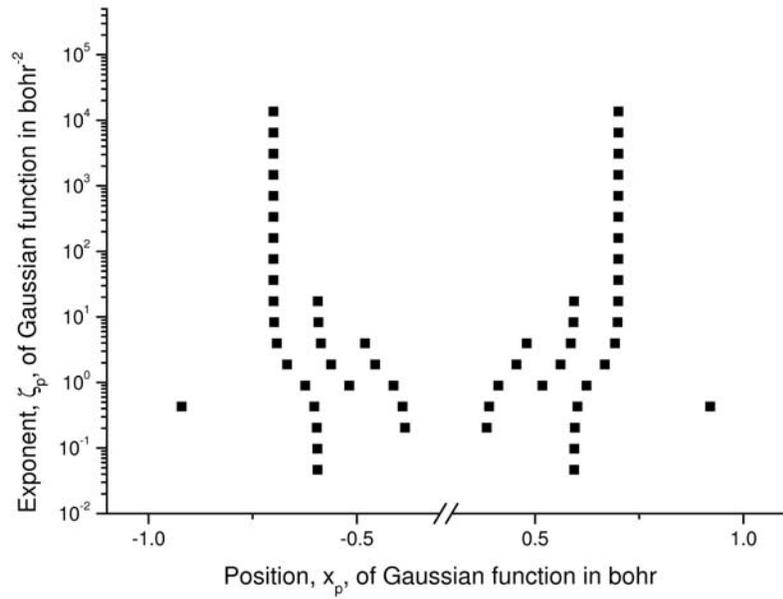


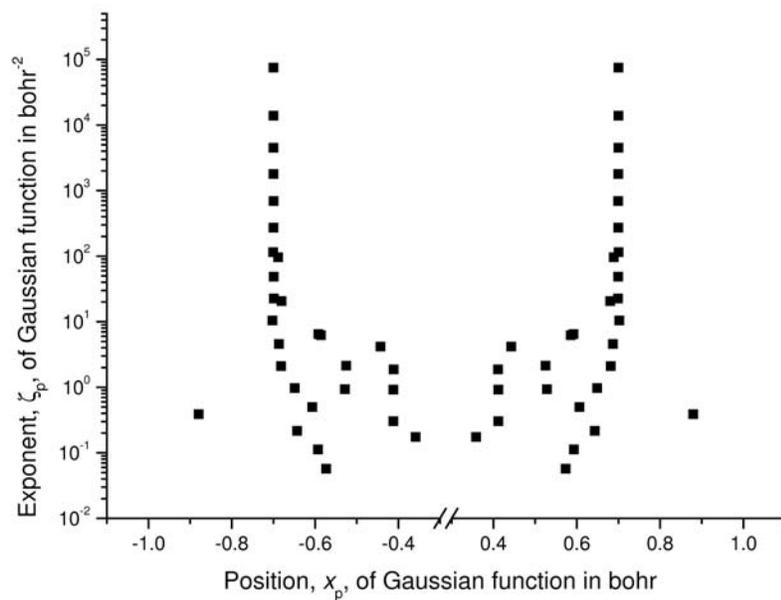
Figure 2. Distributed Gaussian basis set for the ground state of the H<sub>2</sub> molecule for an internuclear distance,  $R$ , of 4.0 bohr with fully optimized exponents and basis function positions. The nuclei are located at  $\pm 0.7$  bohr.

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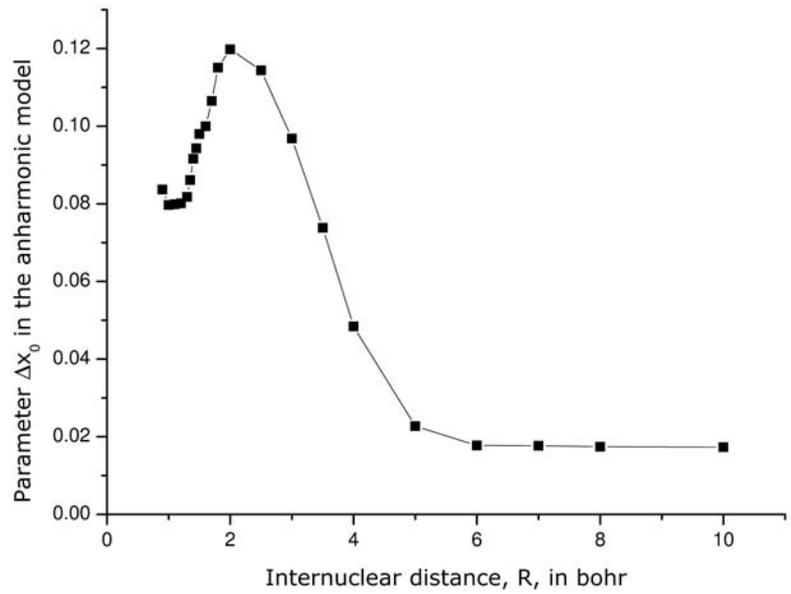
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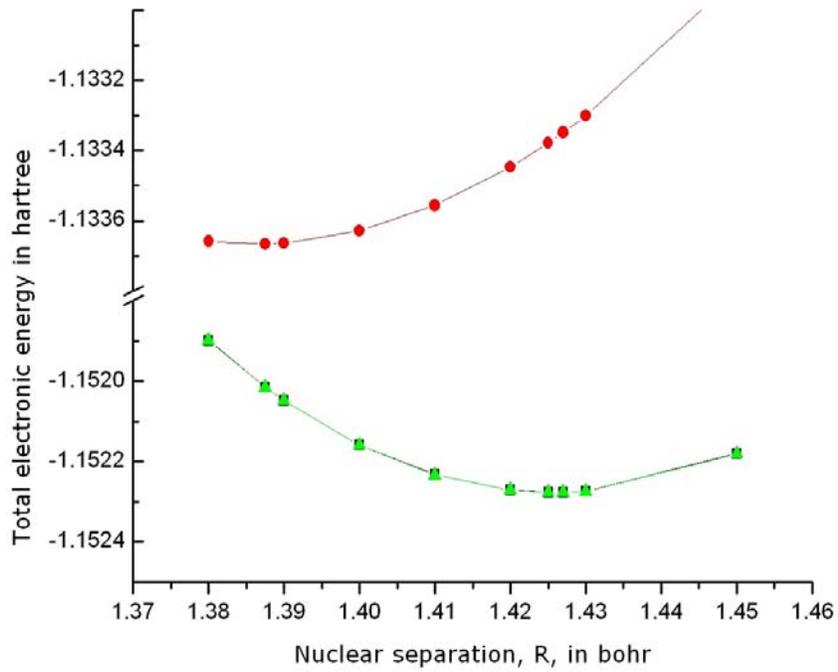
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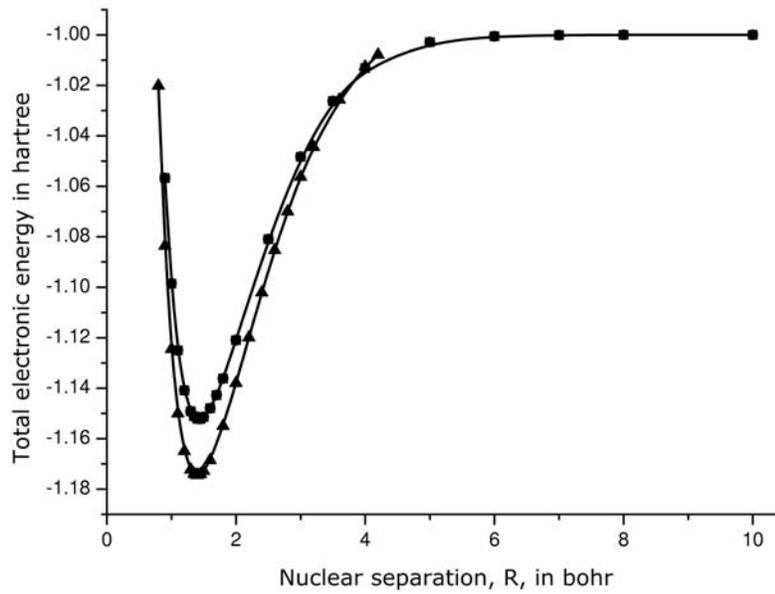


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