Effects of Exchange on Equilibrium Bond Lengths of Heavy, Almost Spherical, Tetrahedral Molecules XH₄

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Abstract

The simplest nonrelativistic density functional theory, namely, that of Thomas, Fermi, and Dirac, is used to study the effect of exchange on the equilibrium bond lengths of heavy tetrahedral molecules XH₄. In particular, the limiting bond length as the central atom X becomes infinitely heavy is shown to be reduced by exchange by some 0.34 Å. Comparison with experiment shows that the main features of the bond-length variation through the series CH₄—PbH₄ are reflected by the Thomas–Fermi–Dirac predictions, though the bond lengths remain too large for finite atomic number Z of the central atom. Therefore, a semiempirical correction is proposed, which, however, tends to zero as Z tends to infinity.

1. Introduction

Analytical progress on the electronic structure of molecules has so far proved notoriously difficult, so that simple models continue to be of interest. In the present work, we return to the use of the Thomas–Fermi model of tetrahedral and octahedral molecules proposed by one of us [1] and developed more recently by Pucci and March [2]. This model has two substantial simplifications underlying it:

(i) The tetrahedral series XH₄ is treated by the so-called one-center expansion method, in which the field of the four protons is expanded in spherical harmonics about the central atom X. In the simplest form of this approach, only the s term is retained [1], so that one is left with a soluble central field problem.

(ii) This central field model is solved self-consistently by the simplest form of density functional theory, namely, the Thomas–Fermi method. Since this approach has its origins in statistical arguments, it will evidently apply best when the central atom X, with atomic number Z say, is heavy. However, only nonrelativistic theory will be used in the present treatment (see, however, some comments in Section 4).

Two important results were then obtained [1], on the basis of the simplifications (i) and (ii) above: namely, analytic formulae for the total energy $E_{TF}$ and its derivative $dE_{TF}/dR$, where R denotes the X—H distance. This framework was utilized by Pucci and March [2] to extract an analytic expression for the bond

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length, $R_e$ say, at equilibrium, in the limit that $Z$ tends to infinity. What is of interest here is that this shows that $R_e$ tends to a finite limit $R_e^0$, which takes the form

$$R_e^0 = \lim_{Z \to \infty} R_e = \frac{12}{\sqrt{12(1 - d)}} \left( \frac{3}{32\pi^2} \right)^{2/3} \frac{h^2}{2me^2} = 2.68 \text{ Å},$$

with a geometrical factor $d = (3 - \sqrt{6})/32$ for tetrahedral molecules. Although in the present work we shall present values of $R_e$ obtained numerically for $Z = 6$ (CH$_4$), $Z = 14$ (SiH$_4$), etc., up to $Z = 114$, our basic concern is with the effect of exchange on the limiting value (1).

A start on the program of including exchange was made by Ballinger and March [3], who estimated the exchange energy [4],

$$A = -c_e \int [\rho(r)]^{4/3} dr, \quad c_e = \frac{3}{4} e^2 \left( \frac{3}{\pi} \right)^{1/3},$$

for CH$_4$ and SiH$_4$. The present work generalizes this study and, in particular, makes some analytic progress in evaluating the effect of exchange in this Thomas–Fermi–Dirac (TFD) model in the limit $Z$ that tends to infinity.

We want to point out that in this inclusion of exchange the density from the original Thomas–Fermi model is used; that is, the variational foundation of the Thomas–Fermi–Dirac model is exploited. In other words, the effect of exchange on the ground-state density is not studied; the total energy is merely evaluated as

$$E_{TFD} = E_{TF} + A_{TF},$$

where $E_{TF}$ is precisely as in [1], while $A_{TF}$ is calculated from Eq. (2) with the Thomas–Fermi density inserted for $\rho(r)$. Evidently, the equilibrium bond length, our prime concern here, is found by minimizing the energy in Eq. (3) with respect to the X–H distance $R$, to yield the implicit equation determining $R_e$ as

$$\left. \frac{dE_{TFD}}{dR} \right|_{R_e} = \left. \frac{dE_{TF}}{dR} \right|_{R_e} + \left. \frac{dA_{TF}}{dR} \right|_{R_e} = 0.$$

Since, as already mentioned, a formula was obtained in [1] for $dE_{TF}/dR$ in terms of the self-consistent Thomas–Fermi solutions for density and potential field, the main concern here is with a full study of $dA_{TF}/dR$ for the XH$_4$ series over a substantial range of atomic number $Z$ of the central atom X.

2. Derivative of Exchange Energy $A_{TF}$ with Respect to the X–H Bond Length

As usual in Thomas–Fermi theory, we work with the “screening” function $\phi(x)$, which is related to the self-consistent potential energy $V(r)$ by

$$V(r) = -\frac{Ze^2}{r} \phi(x), \quad r = bx, \quad b = 0.88534a_0/Z^{1/3},$$

where $a_0$ is the Bohr radius $h^2/me^2$. Evidently, $\phi(x)$ is now dependent on the bond length $R$, which is expressed in terms of the dimensionless quantity $S$ with
\( R = bS \). Thus, one can rewrite Eq. (2) in terms of \( \phi \) in Eq. (5) as

\[
A_{1\beta} = -0.36Z^2 \int_0^\infty \phi^2 \, dx. \tag{6}
\]

According to Eq. (4), we can now focus on the derivative \( dA/dR \), and defining

\[
I = \int_0^\infty \phi^2 \, dx, \tag{7}
\]

the quantity \( dI/dS \) is the basic object needed to evaluate the equilibrium bond length \( R_e \).

Since, in the one-center expansion simplified as in Eq. (5) above, the electric field suffers an appropriate discontinuity across the spherical surface distribution of radius \( R \) representing the effect of the protons in this model and since \( \phi'(x, S) \) is discontinuous, and, thus, with region 1 dealing with \( 0 < x < S \) and region 2 corresponding to \( x \geq S \), one can write \( I \) in Eq. (7) as

\[
I = I_1 + I_2 = \int_0^S \phi_1(x, S)^2 \, dx + \int_S^\infty \phi_2(x, S)^2 \, dx. \tag{8}
\]

Differentiating partially with respect to \( S \) then yields, because \( \phi \) is continuous at \( x = S \), only its slope \( \phi' \) having a discontinuity:

\[
\frac{dI}{dS} = 2 \int_0^S \phi_1(x, S) \frac{\partial \phi_1}{\partial S} \, dx + 2 \int_S^\infty \phi_2(x, S) \frac{\partial \phi_2}{\partial S} \, dx. \tag{9}
\]

One can use the Coulson-March [5] series solution to represent \( \phi_2 \) appearing in Eq. (9):

\[
\frac{\phi_2(x)}{x^c} = \frac{144}{x^3} \left[ 1 - \frac{F_1}{x^c} + \frac{F_2}{x^{2c}} - \frac{F_3}{x^{3c}} + \ldots \right], \tag{10}
\]

where \( F_n = f_n F_1^n \) and \( c = (\sqrt{73} - 7)/2 \). The value of \( F_1 \) must, evidently, be obtained as a function of \( S \) by matching correctly on to the appropriate solution \( \phi_1(x, S) \) in region 1 (see Section 3 below). This suggests that one works with Eq. (9) in the modified form

\[
\frac{dI}{dS} = 2 \frac{da_2}{dS} \int_0^S \phi_1 \frac{\partial \phi_1(x, S)}{\partial a_2} \, dx + 2 \frac{dF_1}{dS} \int_0^\infty \phi_2 \frac{\partial \phi_2(x, S)}{\partial F_1} \, dx. \tag{11}
\]

This equation suggests that the simplest way to get insight as to the relative magnitudes of the two terms in Eq. (9) is to study \( da_2/dS \) and \( dF_1/dS \), where \( a_2 \) is the slope of \( \phi_1(x, S) \) at the origin \( x = 0 \).

3. Explicit Equilibrium Bond Lengths for the XH\(_4\) Series and Limiting Bond Lengths

To evaluate the quantities appearing in Eq. (11), it is necessary to construct two curves \( \phi_1(x) \) and \( \phi_2(x) \), intersecting at the point \( x = S \), and the similar curves, intersecting at the point \( x = S + \Delta S \) (where \( \Delta S \) is small). The conditions
to be satisfied by the functions at the intersection point are as follows:

\[
\phi_1(S) = \phi_2(S) ;
\]

\[
\frac{d\phi_1}{dx} \bigg|_S = \frac{d\phi_2}{dx} \bigg|_S + \frac{N}{SZ};
\]

where \( N = 4 \) for \( \text{XH}_4 \) molecules. Hence, one must adjust the initial slope \( a_2 \) and the value of \( F_1 \) in order to satisfy these conditions. It is convenient to define a function

\[
Y = \sqrt{(\phi_1(S) - \phi_2(S))^2 + (\phi_1'(S) - \phi_2'(S) - \frac{N}{SZ})^2}
\]

(12)

and to find its minimum with respect to the parameters \( a_2 \) and \( F_1 \) for the fixed values of \( S \). For the purpose of minimization, the quasi-Newton algorithm can be used, as it requires the values of the function only.

Using the curves obtained in this way, it is possible to evaluate \( \frac{d\phi_2}{dx} \) and \( \frac{dF_1}{dx} \). The numerical results obtained for the \( \text{XH}_4 \) series proved that the former is negligible compared to the latter. This fact was used (see Appendix A) to get an approximate analytical expression for \( \frac{dA_{\mu}}{dx} \).

For each molecule in the \( \text{XH}_4 \) series, the values of \( \frac{dE_{\mu}}{dx} \) and \( \frac{dA_{\mu}}{dx} \) were evaluated for several values of \( S \) and the absolute values of these derivatives were plotted vs. \( S \). It is clear from Eq. (4) that the intersection of these two curves corresponds to the equilibrium bond length \( R_e \). The values of \( R_e \) were obtained for \( Z = 6 (\text{CH}_4) \), \( Z = 14 (\text{SiH}_4) \), etc., up to \( Z = 114 \). This last case was included, as there are some indications in the literature [6] that a nucleus with \( Z = 114 \) belongs to the "island of stability."

Table I lists the bond lengths calculated in Thomas–Fermi–Dirac (TFD) approximation for comparison with the experimental [7] values. It is easy to see from Figure 1 that exchange reduces the TF equilibrium bond lengths* and thus brings them substantially closer to the observed values.

It is of interest to determine the asymptotic behavior of \( R_{\mu}^{\text{TF}} \) in the limit \( Z \) that tends to infinity. To do so, one needs to obtain an approximate analytic expres-

<table>
<thead>
<tr>
<th>Atomic no. Z of X</th>
<th>( R_e^{\text{TF}} ) (Å)</th>
<th>( R_e^{\text{EX}} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1.094</td>
<td>1.27</td>
</tr>
<tr>
<td>14</td>
<td>1.480</td>
<td>1.57</td>
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<tr>
<td>32</td>
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<td>1.80</td>
</tr>
<tr>
<td>50</td>
<td>1.701</td>
<td>1.92</td>
</tr>
<tr>
<td>82</td>
<td>1.839</td>
<td>2.06</td>
</tr>
<tr>
<td>114</td>
<td></td>
<td>2.19</td>
</tr>
</tbody>
</table>

*In Figure 1, our numerical calculations for the Thomas–Fermi case without exchange exceed the value (1) by some 4%.
Figure 1. Shows equilibrium bond lengths in Å of series XH₄.

Equation for $dA''/dS$ as a function of $Z$ and $R_e$. Inserting all numerical values in Eq. (19) (see Appendix A), one can write for the case of tetrahedral molecules:

$$
\frac{dA''}{dS} = \frac{a}{Z^{\frac{1}{3}}R_e^{5+c}} \left( \frac{dF_1}{dS} \right) + \frac{bF_1}{Z^{\frac{2}{3}}R_e^{5+2c}},
$$

with $a = 1173$ and $b = 1854$. The dependence of $dF_1/dS$ on $Z$ (see Fig. 2) can be well represented by the formula

$$
\frac{dF_1}{dS} = -fZ^{-1/3}, \quad f = 1.268.
$$

Writing the expression for $dE''/dS$ in the form similar to (13), namely,

$$
\frac{dE''}{dS} = \frac{N^2(1 - d)\alpha}{Z^{1/3}R_e^2} - \frac{4 \times 144N\alpha^4}{Z^{1/3}R_e^5}; \quad \alpha = 0.88534
$$

and inserting it into (4) gives in the limit $Z \to \infty$:

$$
10.91R_e^{0.178} - 1415.54R_e^{0.5} + 1487.80 = 0.
$$

From this equation, one can obtain the limiting equilibrium bond length: $R_e^0 = 2.34$ Å. This value is 0.34 Å lower than that obtained in the work of Pucci and March [2], which neglected exchange energy.
Figure 2. Shows variation of $dF_1/dS$ with atomic number $Z$ of central atom, with $F_1$ as in Eq. (10).

4. Comparison with Experiment and Summary

The results for $R_e$ vs. $Z$ plotted in Figure 1 for the almost spherical tetrahedral molecules are compared with the experimental results in Table I. It can be seen that the error increases in passing from silane to germane, which at first sight seems surprising in view of the fact that the Thomas–Fermi method should become more reliable as the number of electrons increases. Heath et al. [8], however, have concluded previously from a study of regularities in bond lengths for a number of molecules that the bond in germane is probably "abnormally short and strong." The Thomas–Fermi bond lengths, as already noted for CH$_4$ and SiH$_4$ by Ballinger and March [3], are too long, even though inclusion of exchange considerably improves the agreement between theory and experiment. Even for the heaviest molecule for which the equilibrium bond length is available from experiment, namely PbH$_4$, there is still a substantial discrepancy between theory and experiment.

One may therefore inquire as to the origin of this discrepancy, three questions being raised below that are relevant:

(a) Will refining the "electron gas" functionals for kinetic and exchange energies, and, hence, improving the self-consistent ground-state density, have a significant effect within the spherical molecular model?

(b) With refined functionals in (a), will inclusion of higher terms in the one-center expansion improve the agreement between observed and calculated bond lengths? We do not presently know a definitive answer to this question. One related point that emerges from our study is that the radial density $D(r) = 4\pi r^2 \rho(r)$ at the position $R_{e\text{rad}}$ of the protons remains remarkably constant through the series SiH$_4$–PbH$_4$.

(c) What will relativistic corrections do to the measured bond length of PbH$_4$; we should really make these before comparing with the results of the present non-
relativistic model. However, other studies (Lohr and Pyykkö [9]) lead one to expect that relativistic effects will make but a small contraction of the nonrelativistic bond lengths, though $Z$ is restricted in relativistic theory by singularities in the Dirac equation ($Z = 137$ for a point nucleus; $Z \approx 170$ for a finite nucleus).

We finally note that there is a useful semiempirical relation by means of which to pass from the TFD equilibrium bond length to the experimental value $R_e$, namely,

$$\frac{1}{R_e} = \frac{1}{R_e^{\text{rel}}} + \frac{0.2}{Z^{0.3}},$$

(17)

where the correction to $R_e^{\text{rel}}$ evidently tends to zero as $Z \to \infty$. The results thereby obtained for $R_e$ are also plotted in Figure 1 to show the quality of this formula (17).

Appendix A. Use of Series (10) for Asymptotic Evaluation of Exchange Energy

In the evaluation of the exchange energy $\Delta''$ for large $S$, one requires the integral $J_2$, say:

$$J_2(S) = \int_{\phi_2(x,S)}^{\delta \phi_2(x,S)} dx.$$

(18)

Here we outline its evaluation using the Coulson-March series solution (10). Inserting this into Eq. (18), the result can be integrated term by term to yield, for the two lowest-order contributions:

$$J_2(S) = - \frac{12^4}{(5 + c)S^{5+c}} + \frac{12^4 \times (2f_2 + F_1)}{(5 + 2c)S^{5+2c}}.$$

(19)

As already mentioned in the text, the reason that $J_1$ corresponding to $I_1$ of the text is small is because $\frac{d a_2}{dS}$ is very small. In principle, one can use Baker's small $x$ expansion to take the derivative of $\phi_1(x,S)$ with respect to $a_2$ but one would not expect the resulting series for $J_1$ to converge usefully for large $S$.

Appendix B. WKB Levels in Thomas–Fermi (TF) Self-consistent Fields for GeH₄

Senatore and March [10] have made an extensive study of the level spectrum of the self-consistent TF potential for neutral atoms in the WKB approximation. The purpose of this Appendix is to study, again using the WKB method, the corresponding level spectrum for the self-consistent fields of XH₄ molecules. The formula employed is explicitly

$$\left( \frac{s + \frac{1}{2}}{2} \right) \hbar = \int_{r_1}^{r_2} \sqrt{\varepsilon_d - V_\tau(r) - \left( \frac{l + \frac{1}{2}}{2} \right) \hbar^2} dr,$$

(20)

A referee has drawn our attention to the recent review by Pyykkö, now recorded in [9]. His estimates of bond-length contractions range from $10^{-4}$ Å for CH₄ to $10^{-1}$ Å for PbH₄.
where \( r_1 \) and \( r_2 \) represent the classical turning points of the motion and the total quantum number \( n \) is related to \( s \) and \( l \) as follows: \( n = s + l + 1 \).

(i) Unscreened Nuclear Field

To illustrate the use of Eq. (20) in a case where some analytical progress proves possible, let us first apply it to the unscreened nuclear potential energy \( V_n(r) \) for the spherical model employed in the present work, namely:

\[
V_n(r) = \begin{cases} 
\frac{-Ze^2}{r} - \frac{Ne^2}{R}, & r \leq R \\
\frac{(Z + N)e^2}{r}, & r > R, 
\end{cases}
\]  

(21)

where \( N = 4 \) for XH\(_4\) molecules.

Let us first assume in Eq. (20) that \( r_2 < R \). Then, one has a solution that is related to the Bohr level spectrum \(-\frac{(Z^2e^2)}{2n^2a_0}\), which is given exactly by Eq. (20), putting \( N = 0 \) in Eq. (21). Evidently,

\[
E_{nWKB} = -\frac{Z^2e^2}{2n^2a_0} - \frac{Ne^2}{R}
\]  

(22)
since the constant \(-Ne^2/R\) is merely added to the Coulomb potential \(-Ze^2/R\) according to the first line of Eq. (21).

Turning to the second case, when \( r_1 > R \), one has the second line only of Eq. (21) and

\[
E_{nWKB} = -\frac{(Z + N)e^2}{(2n)^2a_0}.
\]  

(23)

Evidently, the intermediate case where the limits \( r_1 \) and \( r_2 \) embrace \( R \) needs studying fully. We have not, to date, solved this third case analytically, though it is obviously tractable by the numerical procedure adopted below for the TF self-consistent field for GeH\(_4\) inserted into Eq. (20). We anticipate that a weak dependence on \( l \) will appear in this third regime.

(ii) Eigenvalues for Self-consistent TF Field for GeH\(_4\)

Specifically, we have carried out the calculations for GeH\(_4\) at the TF equilibrium bond length \( R_e = 2.56 \ \text{Å} \). The results are given in Table II along with the "experimental" eigenvalues \([11]\) for Kr, which is the "united atom" limit for GeH\(_4\). The sum of the eigenvalues \( e_{nl} \) over all occupied states can be compared with the TF value for \( E_\Sigma^t = \frac{1}{2}E \), where \( E \) is calculated with the formula given in \([1]\). One knows from the work of Scott \([12]\) and later workers that an important correction, dominated by the K shell of the central X atom, is required, due to pronounced density gradients near the nucleus. Adopting Scott’s atomic value of \( \frac{1}{2}Z^2 \), one finds \( E_S = -1154 \ \text{au} \), which is in fair agreement with the WKB result \( E_S = -1166 \ \text{au} \).
Table II. WKB eigenvalues for GeH₄ in self-consistent Thomas–Fermi field.

<table>
<thead>
<tr>
<th>Energy levels</th>
<th>WKB eigenvalues (Ry)</th>
<th>Eigenvalues for Kr (Ry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>-771.0</td>
<td>-1053.1</td>
</tr>
<tr>
<td>2s</td>
<td>-93.0</td>
<td>-141.5</td>
</tr>
<tr>
<td>2p</td>
<td>-83.0</td>
<td>-124.7</td>
</tr>
<tr>
<td>3s</td>
<td>-12.5</td>
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<tr>
<td>3p</td>
<td>-8.7</td>
<td>-16.0</td>
</tr>
<tr>
<td>3d</td>
<td>-2.6</td>
<td>-6.9</td>
</tr>
<tr>
<td>4s</td>
<td>-0.7</td>
<td>-2.0</td>
</tr>
<tr>
<td>4p</td>
<td>-0.2</td>
<td>-1.0</td>
</tr>
</tbody>
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Bibliography


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