Equilibrium-bond-length predictions of very heavy heteronuclear molecules

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The predictions of a central-field molecular model, designed to represent a series such as CH_4, SiH_4, . . . , PbH_4, are first derived, within a nonrelativistic framework, in the limit in which the nuclear charge Z_2e of the heavier atom is allowed to tend to infinity. It is shown that in this model, in which the four outer protons in PbH_4, say, are smeared uniformly over the surface of a sphere of radius R equal to the Pb–H bond length, the equilibrium bond length R_e can be calculated analytically in the limit as Z_2e tends to infinity. In the series of tetrahedral molecules CH_4, SiH_4, . . . , PbH_4, R_e tends, in fact, to a finite value equal to 2.68 Å. This prediction of a finite asymptotic bond length is then confronted with the experimental facts not only for the series CH_4, SiH_4, . . . , PbH_4, but also for tetrahedral fluorides, chlorides, and bromides, and also for octahedral molecules. The empirical results are entirely consistent with the model prediction of a finite asymptotic limit of the bond length R_e as $Z_2 \rightarrow \infty$. A linear relationship is found between Z_2/R_e and Z_2.

It seems unlikely[1] that there exist any homonuclear chemical systems beyond, say, Pb_2, but it is interesting to inquire whether charge transfer stabilizes heteronuclear molecules.

Our aim, in this paper, has been to extract analytical results in the limit of very heavy heteronuclear molecules, and to this end we have gone back to a rather simple molecular model considered by one of us,[2] and solved by a combination of numerical methods and analysis in the limit where the number of electrons is sufficiently large for the Thomas-Fermi statistical model to be valid.

To be quite specific, consider the series of tetrahedral molecules CH_4 to PbH_4. Because of the high symmetry, one can contemplate expanding the nuclear potential field of the four outer protons about the central nucleus carrying charge Z_2e, say. If one retains only the first (s) term of such an expansion, one is led immediately to the model in which the outer nuclear charges, say with total nuclear charge Z_1e, are spread uniformly over a sphere of radius R equal to, say, the Pb–H bond length.

Within this model, a number of simple results follow.[2] First of all, the total self-consistent potential energy $V(r)$, referred to the nuclear charge Z_2e as origin, can be written in the form

$$V(r) = -\frac{Z_2e^2}{r}\phi(x) \ , \tag{1}$$

where $x = r/b$ ($b = 0.885 Z_2^{-1/3} a_0$) is a dimensionless measure of the distance r from the point charge Z_2e. The dimensionless dependent variable ϕ satisfies the usual nonlinear Thomas-Fermi equation[3]

$$\frac{d^2\phi(x)}{dx^2} = \frac{\phi^{3/2}(x)}{x^{1/2}} \ . \tag{2}$$

Because of the presence of the surface charge at distance $R = bX$ from the origin, the electric field suffers a discontinuity determined by the magnitude of the surface charge density, and this, in turn, is reflected by a discontinuity at X in the derivative of $\phi(x)$, the discontinuity being given precisely by

$$\left.\frac{\partial\phi_1}{\partial x}\right|_{x=X} - \left.\frac{\partial\phi_2}{\partial x}\right|_{x=X} = \frac{Z_1}{XZ_2} \ , \tag{3}$$

where ϕ_1 (ϕ_2) coincides with ϕ for $x < X$ ($> X$) (see March[2]).

But the most important result of Ref. 2 for our purposes is for the equilibrium bond length $R_e = bX_e$, determined by the usual condition $dE/dR\,|_{R=R_e} = 0$, E being the total molecular energy, including of course the nuclear-nuclear potential energy U_{nn} given by

$$U_{nn} = \frac{Z_1e^2}{R}(Z_2 + dZ_1) \ , \tag{4}$$

where d is determined by the molecular geometry and for tetrahedral molecules has the value $d_{\text{tetrahedral}} = 3\sqrt{6}/32$.

As shown by one of us,[2] dE/dR is zero when

$$X_e \left.\frac{\partial\phi_1}{\partial x}\right|_{x=X_e} - \phi_1(X_e) = \frac{dZ_1}{Z_2} \ . \tag{5}$$

Equations (1)–(5) constitute the essential basis for the derivation of the main result of the present paper, namely, an analytical formula for X_e and hence the equilibrium bond length $R_e = bX_e$ in the limiting case when $Z_2 \rightarrow \infty$ for fixed Z_1. To lead into this derivation, the numerical calculations of Ref. 2, which can be presented by plotting X_e vs Z_1/Z_2, leave no doubt that as $Z_1/Z_2 \rightarrow 0$ in accord with the desired limiting process discussed above, $X_e \rightarrow \infty$. It is the detailed way in which X_e goes to infinity which is our main concern in what follows.

As X tends to infinity, we require for $x > X$ a solution ϕ_2 of the Thomas-Fermi Eq. (2) which tends to zero at infinity. In fact, the general form of the solutions of Eq. (2), which tend to zero at infinity, was established by Coulson and March,[4] and their work allows us to write, for suffi-

ciently large x,

$$\phi_2(x)=\frac{144}{x^3}\left[1-\frac{F_1}{x^c}+\cdots\right], \tag{6}$$

where in the present problem, $F_1=F_1(Z_1/Z_2)$ and the exponent c is given by $c=(\sqrt{73}-7)/2=0.772$. Here we shall suppose that X, and hence evidently x, is so large that we can neglect the term in F_1 in Eq. (6). Therefore, inserting the approximation $\phi_2=144/x^3$, valid as $Z_1/Z_2\to 0$, into Eq. (3) we can evidently calculate both $\partial\phi_1/\partial x|_{X_e}$ and $\phi_1(X_e)=\phi_2(X_e)$ entering the equilibrium condition (5) and we readily find, in the limit $Z_1/Z_2\to 0$:

$$X_e^0=\left(\frac{Z_2}{Z_1}\right)^{1/3}\frac{12}{[3(1-d)]^{1/3}}, \tag{7}$$

confirming the assertion made above that $X_e\to\infty$ as $Z_2\to\infty$ for finite fixed Z_1. Forming the asymptotic equilibrium bond length $R_e^0=bX_e^0$ in this same limit, we find that Z_2 cancels out and we are left with the finite equilibrium bond length as $Z_1/Z_2\to 0$:

$$R_e^0=\frac{1}{Z_1^{1/3}}\frac{12}{[3(1-d)]^{1/3}}\left(\frac{3}{32\pi^2}\right)^{2/3}\frac{h^2}{2me^2}. \tag{8}$$

In this molecular model, therefore, the limiting bond length is determined solely by the total nuclear charge Z_1e of the outer atoms and the geometrical factor d. As a numerical example, we take the tetrahedral series $CH_4,\ldots,PbH_4$, when $Z_1=4$. The numerical value of R_e^0 from Eq. (8) is 2.68 Å.

We now establish the limiting law for the way the asymptotic value, R_e^0, given in Eq. (8) is approached according to the above-described model. The procedure is to utilize the series (6), but now including the term F_1/x^c. We must note that, in representing the solution ϕ_2 by the series (6), we must recognize that the dimensionless bond length X must be large, and that F_1 will depend on Z_1/Z_2 and the geometric factor d. However, we are concerned merely with the approach to the limit $Z_2/Z_1\to\infty$.

Using Eq. (6) to the order displayed, we calculate $\partial\phi_1/\partial x|_X$ from the condition (3). Since $\phi_1(X)=\phi_2(X)$, we can then utilize these results in the equilibrium condition (5). This condition then reads

$$\frac{-4\times 144}{X_e^3}+\frac{144F_1(4+c)}{X_e^{3+c}}+\frac{Z_1}{Z_2}(1-d)=0. \tag{9}$$

If we neglect the term in F_1, we regain the limiting value $X_e\to X_e^0$ given by Eq. (7). However, to get the next approximation, we shall write $X_e=X_e^0+\delta$ and inserting this into Eq. (9) we can solve to first order in δ to obtain

$$X_e=X_e^0\left(1+\frac{\delta}{X_e^0}\right)=X_e^0\left(1-\frac{F_1^0(4+c)}{12(X_e^0)^c}+\cdots\right). \tag{10}$$

The quantity F_1^0 denotes the fact that we must calculate F_1 in the asymptotic limit $Z_1/Z_2\to 0$ and this then becomes the neutral atom value, which is known[3] to be 13.27.

Thus, the conclusion is that the asymptotic finite value R_e^0 in Eq. (8) is approached, according to the law

$$R_e=R_e^0\left(1-\frac{F_1^0(4+c)}{12(X_e^0)^c}+\cdots\right), \tag{11}$$

where X_e^0 is given explicitly by Eq. (7). We must caution that this formula is only useful for the model when $Z_1/Z_2\ll 1$.

We have made some estimates on the series CH_4-SnH_4 using empirical bond length data.[5,6] The approach to the asymptotic bond length can be represented, as in the plot of Fig. 1 by

$$\frac{Z_2}{R_e}=\frac{Z_2}{R_e^0}\left(1+\frac{A}{Z_2^{c/3}}+\cdots\right) \tag{12}$$

according to the model. However, if we fix the exponent of Z_2 in fitting the empirical data as $c/3\simeq 0.257$, then for the CH_4-SnH_4 data, A is found to be ~ 1.8, whereas the prediction of this work from the molecular model would give $A\sim 1.4$. The model seems therefore to predict the approach to the limiting law semiquantitatively. We have no way, at present, of deciding if some improvement can be achieved by including the higher terms in the one-center expansion or by considering the relativistic corrections which naturally would be reflected in the empirical data, but are not in the model which is purely nonrelativistic. We suspect, however, that the main effect lies in truncating the one-center expansion at the first term.

It is of obvious interest to enquire also whether the experiment indicates agreement, or otherwise, with the model prediction (8), that the equilibrium bond length R_e tends to a finite asymptotic value as $Z_1/Z_2\to 0$.

We have found it convenient, in analyzing available empirical data on bond lengths of tetrahedral molecules, to plot Z_2/R_e vs Z_2, such as has been shown in Fig. 1 for CH_4, SiH_4, GeH_4, and SnH_4. The theoretical prediction corresponding to Eq. (8) with $Z_1=4$ is shown by the dashed curve in Fig. 1. Though the present work is entirely nonrelativistic, our attention has subsequently been drawn to relativistic calculations by Lohr and Pyykkö,[7] which also display such a limiting value of R_e, though from purely numerical studies.

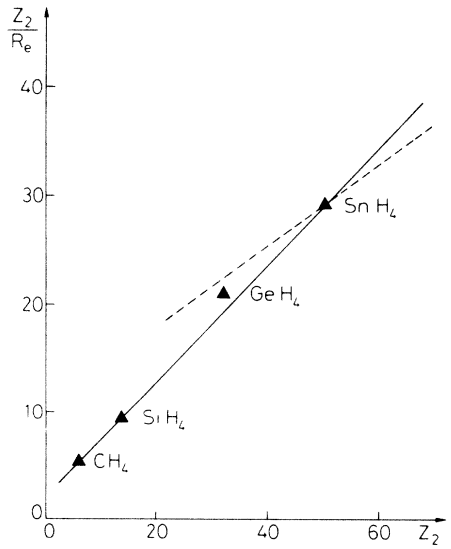

FIG. 1. Plot of Z_2/R_e vs Z_2 for series $CH_4,\ldots,SnH_4$. The dashed curve shows the asymptote predicted by formula (8). The experimental values of R_e (in Å) have been taken from Refs. 5 and 6.

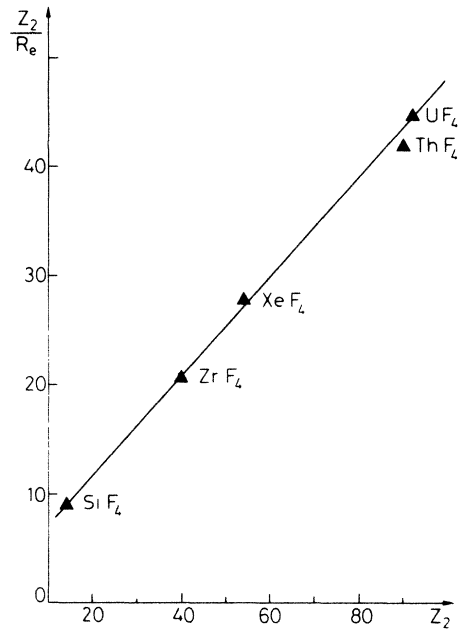

FIG. 2. Plot of Z_2/R_e vs Z_2 for tetrahedral fluorides. The experimental values of R_e (in Å) have been taken from Ref. 6.

Because of the encouraging results in Fig. 1, which appear entirely consistent with the model prediction of a finite asymptotic bond length, we have also made similar plots for tetrahedral fluorides, chlorides, and bromides in Figs. 2–4.

Comparing these three figures, it is possible to draw straight lines if we neglect the heaviest elements U and Th in each case. From the slopes of these straight lines, the bond lengths obtained are 2.2, 2.4, and 2.5 Å for F, Cl, and Br series, respectively. However, since the model prediction concerns the limit $Z_2 \rightarrow \infty$, it could be argued that a more plausible slope is that obtained from the heaviest elements U and Th. These lead to bond lengths of 0.8, 1.4, and 1.3 Å for F, Cl, and Br series, respectively. Returning to the theoretical prediction in Eq. (8), we find with Z_1 the bare nuclear charges, i.e., $Z_1 = 36$, 68, and 140 for F, Cl, and Br series, respectively, the values $R_e^0 = 1.3$, 1.0, and 0.8 Å. Again, the available evidence seems to support the theoretical prediction of a finite asymptotic value of R_e.

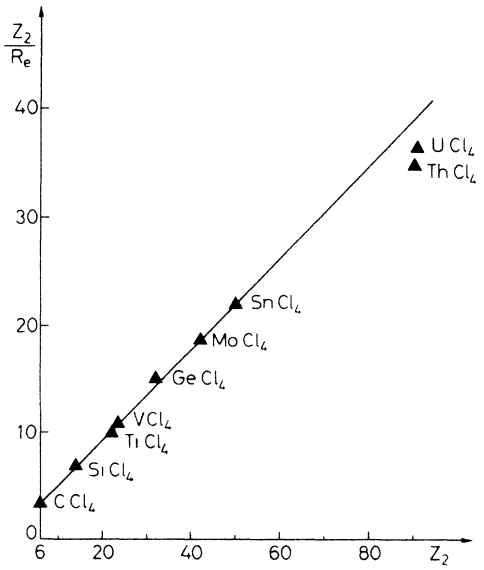

FIG. 3. Same as Fig. 2, but for chlorides.

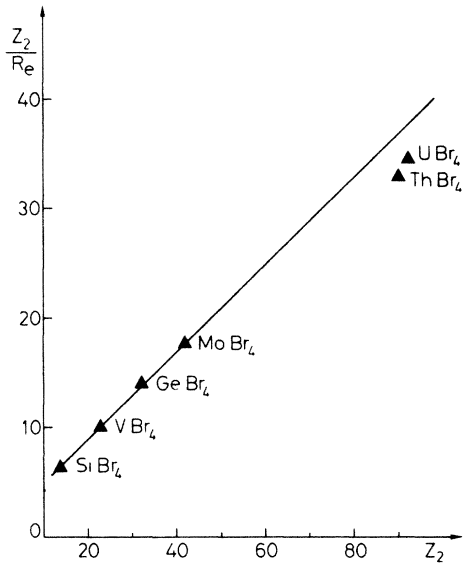

FIG. 4. Same as Fig. 2, but for bromides.

We have also studied the empirical data on octahedral molecules, for which d in Eq. (4) is given by $d_{\text{octahedral}} = (1+4\sqrt{2})/24$. As for tetrahedral molecules, if one ignores U, Np, and Pu, a straight line can be drawn, as is seen in Fig. 5, with slope corresponding to a bond length

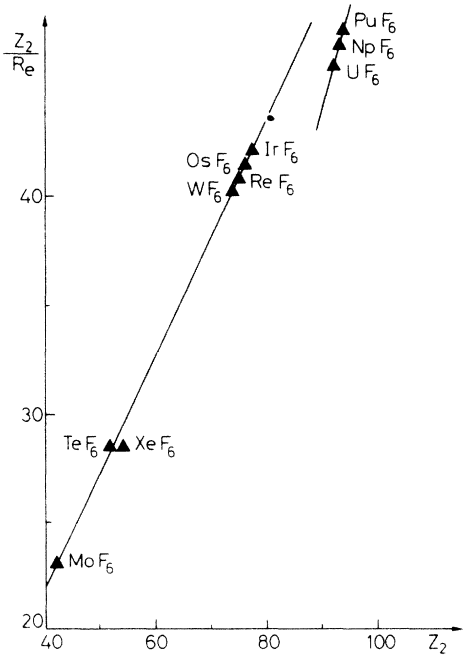

FIG. 5. Plot of Z_2/R_e vs Z_2 for octahedral molecules. The experimental values of R_e (in Å) have been taken from Ref. 6.

of 2.0 Å. However, as discussed previously, the limit $Z_2 \rightarrow \infty$ can be argued to more nearly correspond to the slope of the line through the three heaviest elements U, Np, and Pu. This yields an asymptotic bond length of 1.2 Å. Taking the theoretical prediction (8) with the bare nuclear charge $Z_1 = 54$, we find $R_e^0 = 1.1$ Å.

In summary, the most remarkable finding of the present work is that in the above-described molecular model the limiting value of the equilibrium bond length tends to a finite value, involving the "geometric constant" d appearing in the nuclear-nuclear potential energy (4).

Furthermore, for the series $CH_4, \ldots, PbH_4$, which seems the most appropriate for the model prediction to be tested, it seems possible, though it has not been demonstrated, that the model prediction may be quantitatively correct. Even for molecules with atoms with well defined cores in the outer positions, e.g., UF_6, it seems still possible that the model prediction of a finite asymptotic bond length is quantitatively correct.

In conclusion, though it seems unlikely that there will be any homonuclear chemistry beyond, say Pb_2, charge transfer stabilizes heteronuclear molecules. The present paper, therefore, makes a start on at least some aspects of the theoretical chemistry of very heavy heteronuclear molecules.

[1]J. F. Mucci and N. H. March, J. Chem. Phys. **82**, 5099 (1985).
[2]N. H. March, Proc. Cambridge Philos. Soc. **43**, 665 (1952).
[3]See, for example, N. H. March, in *Theory of the Inhomogeneous Electron Gas,* edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).
[4]C. A. Coulson and N. H. March, Proc. Phys. Soc. London, Sect. A **63**, 367 (1950).
[5]*CRC Handbook of Chemistry and Physics,* edited by R. C. Weast (CRC Press, Palm Beach, 1979).
[6]*Structure Data of Free Polyatomic Molecules,* edited by K. H. Hellewege (Springer, Berlin, 1976), Vol. II, p. 7.
[7]L. L. Lohr and P. Pyykkö, Chem. Phys. Lett. **62**, 333 (1979).