Brief Reports

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Relativistic correction to equilibrium bond lengths for heavy, almost spherical molecules

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The relativistic correction to the limiting bond length found by Pucci and March for heavy, almost spherical molecules typified by the series $CH_4, \ldots, PbH_4$ is calculated as a function of the fine-structure constant α by means of relativistic Thomas-Fermi theory. The correction is found to remain nonzero in the limit as the atomic number of the central atom X in the XH_4 series tends to infinity. However, putting $\alpha=\frac{1}{137}$, the numerical change in bond length is extremely small.

I. INTRODUCTION

Recently Pucci and March[1] have shown that for the molecules XH_4 and other related tetrahedral and octahedral systems, the equilibrium bond length R_e tends to a finite limit as the atomic number, Z_2 say, of the central atom X tends to infinity. Their work was nonrelativistic and used the self-consistent Thomas-Fermi theory which is valid in the limit as the number of electrons in the molecule tends to infinity. However, for heavy molecules such as they considered, relativistic corrections are expected to enter the theory, and the purpose of this note is to present the results for the bond length R_e as a function of the fine-structure constant $\alpha=e^2/\hbar c$ obtained by combining the relativistic Thomas-Fermi theory of Vallarta and Rosen[2] with the one-center molecular model of the writer.[3]

In this model the potential energy $V(r)$, measured relative to the chemical potential μ, can be expressed in the dimensionless form

$$\mu - V = \frac{Z_2}{r} e^2 \phi(x) , \tag{1.1}$$

where x measures the distance r from the central nucleus X through

$$r = bx, \quad b = (3/32\pi^2)^{2/3} 2\pi^2 a_0 / Z_2^{1/3}, \quad a_0 = \hbar^2/me^2 . \tag{1.2}$$

The dimensionless "screening function" $\phi(x)$ satisfies now the relativistic Thomas-Fermi equation

$$\frac{d^2\phi}{dx^2} = \frac{\phi^{3/2}}{x^{1/2}} \left[1 + \lambda \frac{\phi}{x} \right]^{3/2} , \qquad \lambda = (4/3\pi)^{2/3} \alpha^2 Z_2^{4/3} . \tag{1.3}$$

This equation (1.3) must be solved in region 1, defined by $0 < r \leq R_e$ for $\phi_1(x)$ and in region 2, $r > R_e$, for $\phi_2(x)$, subject to the condition that there is a discontinuity in electric field across the surface charge distribution at $R_e = bX_e$, given by[3]

$$\left[\frac{d\phi_1}{dx} \right]_{X_e} - \left[\frac{d\phi_2}{dx} \right]_{X_e} = \frac{Z_1}{X_e Z_2} , \tag{1.4}$$

where $Z_1 e$ is the total nuclear charge on the outer atoms, i.e., $4e$ for the series XH_4.

Senatore and March[4] have shown that there is an exact solution of Eq. (1.3), which tends to zero at infinity, having the form

$$\phi_2(x) = \frac{144}{x^3} f(\lambda/x^4) , \tag{1.5}$$

and since ϕ itself is continuous at X_e we can use Eq. (1.4) to obtain the derivative $(d\phi_1/dx)_{X_e}$.

Making use of the Hellmann-Feynman theorem, we can write at equilibrium[3]

$$X_e \left[\frac{d\phi_1}{dx} \right]_{X_e} - \phi_1(X_e) = \frac{Z_1 d}{Z_2} , \tag{1.6}$$

where d is a geometrical factor, having the values

$$d = 3\frac{\sqrt{6}}{24} \tag{1.7}$$

for tetrahedral molecules and

$$d = \frac{1+4\sqrt{2}}{24} \tag{1.8}$$

for octahedral molecules.

Inserting Eq. (1.5), valid as X_e tends to infinity, into Eqs. (1.4) and (1.6), we find for R_e, as Z_2 becomes large,

$$X_e^3=4\times 144\frac{[f(s_e)+s_e f'(s_e)]}{(1-d)Z_1}Z_2,\quad s_e=\lambda/X_e^4\ . \tag{1.9}$$

This equation (1.9), when combined with the series solution for $f(s)$ in Eq. (1.5) calculated explicitly by Senatore and March,[4] constitutes the main result of the present paper. The aim of Sec. II is to describe on this basis the variation of the equilibrium bond length R_e with fine-structure constant α.

II. RELATIVISTIC CORRECTION TO LIMITING BOND LENGTH

If we had set $\alpha=0$ at the outset, then the function $f(s)$ in Eq. (1.5) would be replaced by unity and Eq. (1.9) leads back immediately to the result of Pucci and March.[1] Our object here is to discuss the variation of R_e with the fine-structure constant α.

Following Senatore and March[4] we write a new independent variable $t=a_1 s$, with $a_1=3\times 12^3/76$. Then $f(s)\rightarrow F(t)$ and we have

$$F(t)=\sum_{n=0}^{\infty} f_n t^n \tag{2.1}$$

with the coefficients given explicitly up to $n=13$. In terms of $t_e=a_1 s_e$, Eq. (1.9) now becomes

$$t_e^{3/4}[F(t_e)+t_e F'(t_e)]=\frac{a_1^{3/4}(4/3\pi)^{1/2}\alpha^{3/2}(1-d)Z_1}{576}\ . \tag{2.2}$$

The function $F(t)$ has, in fact, a simple pole at[4] $t_c=0.958\,38$ or $s_c=0.014\,050$.

We have calculated values of the left-hand side of Eq. (2.2) for a series of values of t. For XH_4 molecules, with $Z_1=4$, and d given by Eq. (1.7), a numerical example is $t=0.1$, when the left-hand side of Eq. (2.2) has the value 0.22. This corresponds to an (unrealistic) $\alpha=2$ and an equilibrium bond length $R_e=3.8$ Å. It soon becomes plain that for the true value $\alpha=\frac{1}{137}$, the relativistic correction to R_e, though nonzero in the limit when the atomic number of the central atom tends to infinity, is numerically entirely negligible, and that the limiting bond length of Pucci and March[1] remains fully quantitative in the presence of the relativistic corrections predicted by the Vallarta-Rosen statistical theory. Though results have been obtained by Dirac-Fock theory which lead to small reductions in R_e due to relativity,[5] we expect the predictions of relativistic Thomas-Fermi theory to yield the correct limiting bond length in the limit considered here in which Z_2 tends to infinity. No such limit would exist in Dirac-Fock theory, so comparison is obviously precluded.

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