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Commentationes

Three-Dimensional Bond-Charge Models for Potential Curves of Diatomic Molecules*

George A. Henderson** and Robert G. Parr
Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

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Several simple three-dimensional Fermi-gas models for potential energy curves of diatomic molecules are suggested. Bond-charge parameters close to those predicted by the earlier point bond-charge model of Borkman, Simons and Parr [J. Chem. Phys. **49**, 1055 (1968); **50**, 58 (1969)] are obtained for models assuming uniform spherical or elliptical electron distributions in the bond region.

Key words: Potential curves – Bond-charge – Fermi-gas

1. Introduction

The point of departure for this work is the simple bond-charge model for potential curves of diatomic molecules described by Borkman, Simons and Parr [1]. They considered a point charge of magnitude $-qe$ restricted to motion in one dimension over a length νR, where R is the internuclear separation. The kinetic energy of such a charge varies as $1/R^2$ and the electrostatic interaction with two point-charge atoms of charge $Ze = \frac{1}{2}qe$ gives a potential energy varying as $1/R$. This startlingly simple model gives rise to a total electronic energy of the form:

$$W(R) = T(R) + V(R) = W_0 + W_1/R + W_2/R^2 , \tag{1}$$

which reasonably well represents experimental diatomic potential curves near equilibrium. Further, the values of q which result from fitting the model to experiment can be interpreted as bond orders.

Here, we investigate three other simple models, two of which also yield the form Eq. (1). The new models all involve three-dimensional charge distributions. They also employ the assumption that the electronic kinetic energy depends upon the electron density in the same way as in a statistical or Thomas-Fermi theory. That is, a kinetic energy density proportional to the 5/3 power of the density is assumed.

We consider that at every point in coordinate space, momentum states are fully occupied up to the Fermi momentum $P_F = \hbar k_F$, as in a degenerate Fermi

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** Present address: Department of Physics, Southern Illinois University, Edwardsville, Illinois 62025.

gas [2]. This gives the fundamental density-momentum relation

$$\begin{aligned}\varrho(\boldsymbol{r}) &= \sum_s \int d\boldsymbol{k}\, \varphi_k^*(\boldsymbol{r}, s)\, \varphi_k(\boldsymbol{r}, s)\\ &= \frac{2}{(2\pi^3)}\, 4\pi \int_0^{k_F(\boldsymbol{r})} dk k^2\\ \varrho(\boldsymbol{r}) &= \frac{1}{3\pi^2}\, k_F^3(\boldsymbol{r})\,. \end{aligned} \tag{2}$$

The average (kinetic) energy at a point in space is given by

$$T(\boldsymbol{r}) = \frac{\int dE\, E N(E)}{\int dE\, N(E)}\,, \tag{3}$$

where $N(E)$ is the energy distribution function for a non-interacting Fermi gas confined to a volume V and equals

$$N(E)\, dE = \frac{m^{3/2}\, V}{2^{1/2}\pi^2\hbar^3}\, E^{\frac{1}{2}} dE\,, \tag{4}$$

where m is the particle mass. Carrying out the integrations and expressing the result in terms of the Fermi momentum, one obtains

$$T(\boldsymbol{r}) = \frac{3}{5}\,\frac{k_F^2(\boldsymbol{r})}{2m}\,. \tag{5}$$

Thus the total kinetic energy is given by

$$\begin{aligned} T &= \int d\boldsymbol{r}\, \varrho(\boldsymbol{r})\, T(\boldsymbol{r})\\ &= \frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{2/3} \int d\boldsymbol{r}\, \varrho^{5/3}(\boldsymbol{r})\,, \end{aligned} \tag{6}$$

where Eq. (2) has been used. This relation is assumed for all the models discussed here.

2. Spherical Charge Density Model

The first model assumes that the bond charge $-eq$ in a homonuclear diatomic molecule is uniformly distributed in a sphere of radius $\alpha R/2$ located at the center of the bond, while point charges $Ze = \frac{1}{2}qe$ are located at each of the atoms. Thus for the electron density we have

$$\varrho(\boldsymbol{r}) = \varrho_0\, \Theta(\alpha R/2 - r)\,, \tag{7}$$

where ϱ_0 is a constant, r is the radial variable in a spherical coordinate system located at the bond center and

$$\Theta(x) = \begin{cases} 1 & \text{for} \quad x > 0\,,\\ 0 & \text{for} \quad x < 0\,. \end{cases} \tag{8}$$

The constant ϱ_0 is determined by normalization:

$$q = \int d\boldsymbol{r}\, \varrho(\boldsymbol{r}) = \frac{\varrho_0 \pi \alpha^3 R^3}{6}\,. \tag{9}$$

Computing the kinetic energy *via* Eq. (6), we obtain

$$T=\frac{W_2}{R^2}=\frac{h^2}{2m}\left(\frac{3}{2\pi}\right)^{4/3}\frac{q^{5/3}}{\alpha^2R^2}. \tag{10}$$

For the electronic potential energy we obtain

$$V=\frac{W_1}{R}=\begin{cases}\frac{e^2}{R}(Z^2-4Zq) & \text{for} \quad \alpha<1\,,\\ \frac{e^2}{R}\left(Z^2-\frac{2Zq}{\alpha^3}[3\alpha^2-1]\right) & \text{for} \quad \alpha>1\,.\end{cases} \tag{11}$$

The case $\alpha<1$ is equivalent from the point of view of potential energy to the point-charge Borkman-Simons-Parr model. When α exceeds 1, the bond charge density extends beyond the positions of the two atoms and different values of q result. The two parameters q and α are determined from R_e, the experimental equilibrium distance and k_e, the quadratic force constant:

$$\left.\frac{dW}{dR}\right|_{R_e}=0\,;\quad \left.\frac{d^2W}{dR^2}\right|_{R_e}=k_e\,. \tag{12}$$

Values of q and α for the ground states of 17 homonuclear diatomic molecules are presented in Table 1. Figure 1 permits a comparison of these values of q to those obtained from the Borkman-Simons-Parr one-dimensional model and to the simple bond order. It will be seen that the bond charges from the spherical Fermi-gas model are in qualitative agreement with the one-dimensional values but tend to be a bit higher throughout, especially in the neighborhood of N_2. Note also that all values of α exceed 1.

Table 1. Bond charge and size parameters for spherical Fermi-gas model[a]

Molecule	q	α
H_2	1.78	5.24
Li_2	1.15	1.33
B_2	2.16	1.70
C_2	2.79	1.88
N_2	3.49	2.08
O_2	2.84	2.03
F_2	2.17	1.87
Na_2	1.14	1.21
Si_2	2.52	1.24
P_2	3.21	1.33
S_2	3.04	1.35
Cl_2	2.68	1.34
K_2	1.21	1.03
Se_2	3.06	1.23
Br_2	2.76	1.21
Te_2	3.20	1.06
I_2	2.85	1.09

[a] Model of Eqs. (10) and (11) of text. Bond-charge parameter q and sphere-size parameter α determined from Eq. (12) of text.

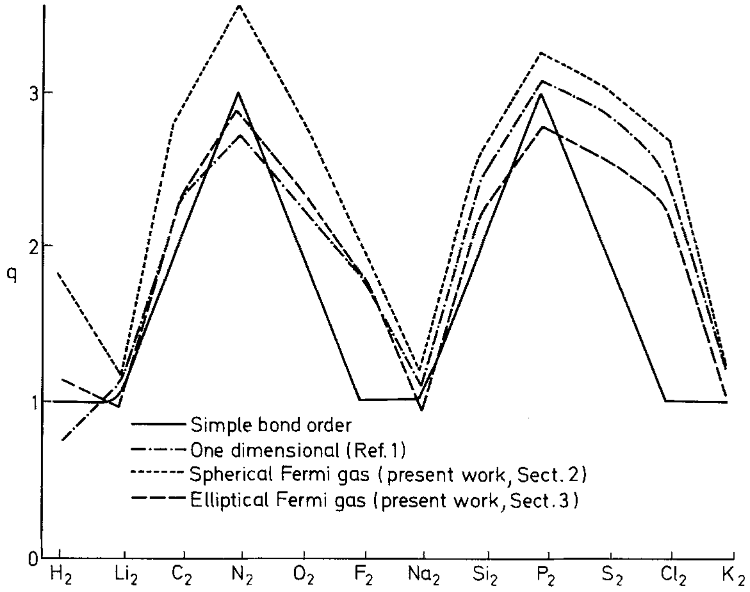

Fig. 1

3. Elliptical Charge Density Model

A potential energy $W(R)$ of the form Eq. (1) also results when one assumes a uniform charge distribution within an ellipsoidal volume. This more nearly represents the shape of a molecular electronic charge distribution. We employ elliptical [prolate spheroidal] coordinates $\xi = \frac{r_A + r_B}{R}$, $\eta = \frac{r_A - r_B}{R}$, and φ, where r_A and r_B are distances from nuclei A and B, respectively, to an arbitrary point in space and φ is an angle of rotation about the bond axis. Since curves of constant ξ are ellipses with foci at atoms A and B, we can employ the step function to cut off the density at a value $\xi = \beta$. Thus we have

$$\varrho(\mathbf{r}) = \varrho_0 \Theta(\beta - \xi), \tag{13}$$

and the charge normalization condition takes the form

$$\begin{aligned} q &= \varrho_0 \int_0^{2\pi} d\varphi \int_{-1}^{1} d\eta \int_1^{\beta} d\xi (\xi^2 - \eta^2) \left(\frac{R}{2}\right)^3 \\ &= \frac{\varrho_0 \pi R^3}{6} (\beta^3 - \beta), \end{aligned} \tag{14}$$

which determines ϱ_0. Proceeding as before, we obtain the electronic kinetic energy expression *via* Eq. (4), yielding

$$T = \frac{W_2}{R^2} = \frac{3h^2}{10m} \left[\frac{9}{4\pi^2(\beta^3 - \beta)}\right]^{2/3} \frac{q^{5/3}}{R^2}. \tag{15}$$

Table 2. Bond charge and size parameters for elliptical Fermi-gas model[a]

Molecule	q	β
H_2	1.13	2.9
Li_2	0.99	1.26
B_2	1.82	1.43
C_2	2.31	1.51
N_2	2.85	1.61
O_2	2.33	1.58
F_2	1.80	1.50
Na_2	0.99	1.21
Si_2	2.19	1.23
P_2	2.77	1.26
S_2	2.62	1.27
Cl_2	2.31	1.27
K_2	1.04	1.14
Se_2	2.65	1.22
Br_2	2.39	1.21
Te_2	2.76	1.16
I_2	2.46	1.17

[a] Model of Eqs. (15) and (16) of text. Bond-charge parameter q and ellipsoid-size parameter β determined from Eq. (12) of text.

The potential energy V_{A_ϱ} due to the interaction of the negative charge distribution with the atomic charge at A is

$$\begin{aligned} V_{A_\varrho} &= -Ze\int dr\,\frac{\varrho(r)}{r_A} = -Ze^2\varrho_0\int_0^{2\pi} d\varphi\int_{-1}^{1} d\eta\int_1^{\beta} d\xi\left(\frac{R}{2}\right)^2(\xi-\eta) \\ &= \frac{-Ze^2\varrho_0\pi R^2}{2}(\beta^2-1)\,. \end{aligned} \tag{16}$$

Atom B experiences the same potential. When one adds the atomic repulsion term, the resulting expression for the potential energy in this model is

$$V = \frac{W_1}{R} = \frac{e^2}{R}\left(Z^2 - \frac{6Zq}{\beta}\right). \tag{17}$$

The values of q and β obtained by fitting the experimental R_e and k_e are displayed in Table 2. Note that the values of β are small enough that (except for H_2) the charge is held rather close to the bond axis. Reference to Fig. 1 shows that the elliptical model gives values of q very close to those obtained by Borkman, Simons and Parr.

4. Elliptical Charge Density Model with Ion Core

As an elaboration of the foregoing two-parameter models, one may consider a three-parameter model which accounts for the finite size of the ion cores by excluding a spherical volume about each atom center from an ellipsoidal charge density allotted to the electrons. Thus the bond charge distribution is constant in an ellipsoidal volume except for two spherical "bubbles" of radius ζ within which it vanishes and it also vanishes outside the ellipsoidal boundary defined by $\xi = \beta$. In terms of step functions, the density for this model is

$$\begin{aligned} \varrho(\xi,\eta) &= \varrho_0\, \Theta(\beta-\xi)\, \Theta(r_A-\zeta)\, \Theta(r_B-\zeta) \\ &= \varrho_0\, \Theta(\beta-\xi)\, \Theta(\tfrac{1}{2}R[\xi+\eta]-\zeta)\, \Theta(\tfrac{1}{2}R[\xi-\eta]-\zeta)\,. \end{aligned} \tag{18}$$

The step functions give integration limits such that

$$\begin{aligned} &1 \leqq \xi \leqq \beta\,; \\ &b-\xi \leqq \eta \leqq \xi - b\,, \qquad b \equiv 2\zeta/R\,. \end{aligned} \tag{19}$$

The bond-charge normalization condition is then

$$\begin{aligned} \int \varrho\, d\tau = q &= \varrho_0 2\pi \left(\frac{R}{2}\right)^3 \int_1^\infty d\xi \int_{-1}^{1} d\eta (\xi^2-\eta^2)\, \Theta(\beta-\xi)\, \Theta(r_A-\zeta)\, \Theta(r_B-\zeta) \\ &= \varrho_0 2\pi \left(\frac{R}{2}\right)^3 \left\{ \int_1^{1+b} d\xi \int_{b-\xi}^{\xi-b} d\eta(\xi^2-\eta^2) + \int_{1+b}^{\beta} d\xi \int_{-1}^{1} d\eta(\xi^2-\eta^2) \right\}, \\ q &= \varrho_0 2\pi \left(\frac{R}{2}\right)^3 (\tfrac{2}{3}[\beta^3-\beta] - \tfrac{4}{3}b^3)\,. \end{aligned} \tag{20}$$

Proceeding as before, the following expression for the electronic kinetic energy is obtained:

$$T = \frac{3h^2}{10m} \left(\frac{9}{4\pi^2}\right)^{2/3} \frac{q^{5/3}}{R^2} ([\beta^3-\beta]-2b^3)^{-2/3}. \tag{21}$$

When the electronic-nuclear attraction potential is evaluated and the ion-core repulsion term is added, one obtains

$$V = \frac{e^2Z^2}{R} - \frac{6Zqe^2}{R} \left[\frac{\beta^2-1-b^2-1/3b^3}{\beta^3-\beta-2b^3} \right]. \tag{22}$$

The denominators in the T and V expressions can be expanded in binomial series to give

$$\begin{aligned} T &= \frac{3h^2}{10m} \left[\frac{9}{4\pi^2(\beta^3-\beta)} \right]^{2/3} \frac{q^{5/3}}{R^2} \left[1 + \frac{32}{3(\beta^3-\beta)} \left(\frac{\zeta}{R}\right)^3 - \frac{640}{3(\beta^3-\beta)^2} \left(\frac{\zeta}{R}\right)^6 + \cdots \right], \\ V &= \frac{Z^2e^2}{R} - \frac{6Zqe^2}{\beta R} \left[1 - \frac{4}{(\beta^2-1)} \left(\frac{\zeta}{R}\right)^2 + \frac{(6-\beta)}{(\beta^3-\beta)} \frac{8}{3} \left(\frac{\zeta}{R}\right)^3 - \cdots \right]. \end{aligned} \tag{23}$$

Thus this model includes higher powers of $(1/R)$ than occur in the earlier models. In particular, the presence of a $(1/R)^3$ term represents a more realistic description of the potential than does the form Eq. (1). One could now proceed to determine β, q, and ζ by fitting to the experimental equilibrium distance, R_e, and the quadratic and cubic force constants k_e and l_e. However, any physically intuitive interpretation of their significance would be partially vitiated by the fact that this model involves a partial contradiction to the virial theorem. If one postulates the general form

$$W(R) = \sum_{n=0}^{\infty} WnR^{-n}, \tag{24}$$

the virial theorem predicts that

$$\begin{aligned} -T &= W + R\frac{dW}{dR} = W_0 - \frac{W_2}{R^2} - \frac{2W_3}{R^3} \cdots - \frac{(n-1)\,W_n}{R^n} - \cdots, \\ V &= 2W + R\frac{dW}{dR} = 2W_0 + \frac{W_1}{R} - \frac{W_3}{R^3} \cdots - \frac{(n-2)\,W_n}{R^n} - \cdots. \end{aligned} \tag{25}$$

Thus while the present three-parameter model gives a correctly behaving energy insofar as V has no $1/R^2$ term and T has no $1/R$ term, it falls short in that T has no $1/R^3$ term.

5. Conclusions

A point of diminishing returns generally is reached when one complicates a simple model too much. Of the models we have here considered we prefer the two-parameter elliptical model of Section 3. Results with it demonstrate that the Borkman-Simons-Parr model can successfully be extended to three dimensions without significant change in the values of (or the interpretation of) the bond charge parameter.

In this work, in order to retain maximum simplicity in extending the point bond-charge model to three dimensions, a uniform density distribution has been assumed. Exploring a more realistic distribution, perhaps closer to a molecular Thomas-Fermi density, could be profitable. Further, the success of Simons [3] in predicting force constants for triatomic molecules using a point charge-point dipole model suggests that suitably simple three-dimensional Fermi-gas models for vibrating polyatomic molecules would be worth examining.

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Professor Robert G. Parr
Department of Chemistry
The Johns Hopkins University
Baltimore, Maryland 21218, USA