

contribution to matrix elements involving particle momenta, or differential operators, may be lost if the sequence of mathematical operations is altered in the calculations.

Our original assertion that in the Born-Oppenheimer approximation the effective Cartesian force constants do not depend upon the nuclear-repulsion energy remains unaffected by these remarks. Because the nuclear-repulsion energy, the first term in (5), is an additive term in the potential function  $U(R)$  and because it satisfies Laplace's equation, it will vanish in the calculation of  $\nabla_{\alpha}^2 U(R_e)$  by any method. Because of this, the effective Cartesian force constants should be of some use in testing molecular wavefunctions. These force constants are well-defined molecular properties whose experimental values are determined directly from Eq. (1) without any special assumptions about the form of the molecular potential function. Further, any ambiguities about what molecular structure to use, the actual experimental structure of that implied by the approximate wavefunction being tested, in comparing experimental and theoretical force constants is essentially eliminated in this case because the Cartesian force constants in (1) do not depend upon the nuclear repulsion energy.

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## Intermolecular Forces in Globular Molecules. VII. The Quadrupole Moment of Benzene\*

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Three estimates of the molecular quadrupole moment of benzene have appeared in the literature, two based on the analysis of second virial coefficients ( $15.7 \times 10^{-26}$  esu<sup>1</sup> and  $15.0 \times 10^{-26}$  esu<sup>2</sup>), and the other on the broadening of the microwave resonance lines of the ammonia inversion spectrum by benzene ( $3.6 \times 10^{-26}$  esu<sup>3</sup>). The large difference between the two sets of values has prompted us to reanalyze the second virial coefficient data including terms arising from the polarizability in the intermolecular potential function

and also to attempt to calculate an independent value of the quadrupole moment of benzene from the anisotropy of its molecular susceptibility.

In the previous analyses of the second-virial-coefficient data the energy of interaction of two benzene molecules was assumed to consist of the interaction of two rigid-point quadrupoles superposed on a spherically symmetric central potential. For the central potential a Lennard-Jones 18-6 potential<sup>1</sup> and the spherical-shell potential<sup>2</sup> were used in the two analyses. In the present work we have retained the spherical-shell potential but superposed on to it the interaction of two anisotropically polarizable quadrupoles. Details of the spherical-shell potential have been given before<sup>4</sup> as have details of the orientation-dependent part of the model.<sup>5</sup> The second virial coefficient for the model is given in Eq. (1),

$$B = b_0 [B_0^*(r_0, T^*) - (112/15)\lambda^2 T^{*-2} H_{10}(r_0^*, T^*) + \dots \\ - 12\alpha^* \lambda T^{*-1} H_8(r_0^*, T^*) \\ + (384/35)\alpha^* K \lambda^2 T^{*-2} H_{12}(r_0^*, T^*) + \dots], \quad (1)$$

in which  $b_0 = \frac{2}{3}\pi N r_0^3$ ,  $T^* = kT/\epsilon$ ,  $r_0^* = r_0 + d$ ,  $\lambda = 3\Theta^2/4\epsilon r_0^5$ ,  $\alpha^* = \bar{\alpha}/r_0^3$ ,  $K = (\alpha_{||} - \alpha_{\perp})/3\bar{\alpha}$ ,  $\bar{\alpha} = (\alpha_{||} + 2\alpha_{\perp})/3$ ,  $\Theta$  is the quadrupole moment of the axially symmetric molecule,  $\alpha_{||}$  and  $\alpha_{\perp}$  are the polarizabilities parallel and perpendicular to the symmetry axis, and  $\epsilon$  and  $r_0$  are parameters characterizing the spherical-shell-potential minimum, the shell having diameter  $d$ .  $B_0^*(r_0^*, T^*)$  and  $H_k(r_0^*, T^*)$  are functions defined and tabulated in previous papers of this series.<sup>2,4</sup>

For benzene we selected the diameter of the spherical shell to be 2.78 Å as before,<sup>2</sup> used experimentally determined<sup>6</sup> values of  $\alpha_{||}$  and  $\alpha_{\perp}$  and chose values of the other three parameters  $\epsilon$ ,  $r_0$ , and  $\Theta$  so as to minimize the quantity

$$\sigma^2 = (N-1)^{-1} \sum_{j=1}^N [\ln B_j(T_j)_{\text{exptl}} - \ln B_j(T_j^*, r_0^*, \Theta)_{\text{calc}}]^2$$

consistent with  $N$  data points. Experimental second virial coefficients in the temperature range 20°–355° were used. Table I contains details of the parameters obtained in the present work and in the previous analysis using the spherical-shell central potential.<sup>2</sup> The best value of the quadrupole moment has been reduced by 20% to  $\pm 12.0 \times 10^{-26}$  esu.

The molecular quadrupole moment of an axially symmetric molecule can be calculated from the formula<sup>7</sup>

$$\Theta = e \left[ \sum_n Z_n (z_n^2 - x_n^2) - (4mc^2/e^2) (\chi_{||} - \chi_{\perp} + \chi_{\text{HF}}) \right], \quad (2)$$

where  $Z_n e$  is the charge on the  $n$ th nucleus at the point  $(x_n, y_n, z_n)$ ,  $m$  and  $e$  are the mass and charge of the electron,  $\chi_{||}$  and  $\chi_{\perp}$  are the magnetic susceptibilities parallel and perpendicular to the axis of symmetry and  $\chi_{\text{HF}}$  is the "high-frequency" contribution to  $\chi_{\perp}$ . The quadrupole moment of benzene could be calculated from Eq. (2) except for the lack of an experimental

TABLE I. Potential parameters for benzene.

	$d$ (Å)	$e/k$ (°K)	$r_0$ (Å)	$\Theta$ (esu)	$\alpha_{\perp}$ (Å <sup>2</sup> )	$\alpha_{\parallel}$ (Å <sup>2</sup> )	$\sigma^2$	Ref. for exptl data
Present work	2.78	605	5.579	$\pm 12 \times 10^{-26}$	123.1 <sup>a</sup>	63.5 <sup>a</sup>	$2.3 \times 10^{-6}$	b
Reference 2	2.78	519	6.050	$\pm 15 \times 10^{-26}$	...	...	$3.2 \times 10^{-6}$	b

<sup>a</sup> Landolt-Börnstein, *Zahlenwerte und Funktionen*, J. Bartels, Ed. (Springer-Verlag, Berlin, 1951), Pt. 3, pp. 510ff.

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value of  $\chi_{HF}$ . However, Weltner<sup>8</sup> has shown that it is possible to estimate  $\chi_{HF}$  for straight-chain paraffin hydrocarbons by assigning a contribution of 4.94 erg G<sup>-2</sup> for each carbon atom and of 2.47 erg G<sup>-2</sup> for each hydrogen atom in a manner analogous to the calculation of the mean magnetic susceptibility of a molecule by Pascal's constants.<sup>9a</sup> In order to obtain an estimate of the quadrupole moment of benzene by this method, we have assumed that  $\chi_{HF}$  for benzene can be calculated by this method. We believe this to be a fair approximation since in the calculation of magnetic susceptibilities from Pascal's constant only a small correction is made for the presence of a benzene ring. Substituting appropriate values in Eq. (2) ( $\chi_{\parallel} = -150.3$  erg G<sup>-2</sup>,  $\chi_{\perp} = -61.5$  erg G<sup>-2</sup>,<sup>9b</sup>  $\zeta_n$  and  $\chi_n$  from bond-length data,<sup>10</sup>  $\zeta_n = 4$  for carbon and 1 for hydrogen) yields a value of  $-11.4 \times 10^{-26}$  esu, thus indicating that the value  $\pm 12.0 \times 10^{-26}$  esu obtained in the present work is probably the most reliable yet available.

The calculations were made on an Elliott-503 computer at the Hydro-University Computer Centre, University of Tasmania.

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## Molecular Intensities from Gaussian Wavefunctions: A Test of the Mixed Oscillator Strength\*

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The use of Gaussian functions has become commonplace in the calculation of molecular energies because of the ease of computing the required energy integrals. It

is of interest to assess the usefulness of Gaussian molecular wavefunctions in computing another, more sensitive quantity, the oscillator strength; and to examine the merits of several formulas available for the computation including one recently suggested by Hansen.<sup>1</sup> In order to do this, the  $1s\sigma$ ,  $2p\sigma_u$ ,  $2p\pi_u$ , and  $3d\pi_g$  states of  $H_2^+$ , and the  $1s\sigma$  and  $2p\sigma$  states of  $HeH^{2+}$  were expanded in a Gaussian lobe basis (GTOL) at various internuclear distances. The oscillator strengths were then calculated for transitions among these states and compared to the exact values.<sup>2-4</sup> The  $H_2^+$  results are also compared to simple LCAO-MO oscillator strengths.<sup>2,3</sup> (See Table I.)

The wavefunctions are represented as

$$\psi = \sum_{i=1}^n c_i \phi_i,$$

where  $\phi_i = \exp[-\alpha_i(\mathbf{r} - \mathbf{r}_i)^2]$ , and  $\mathbf{r}_i$  is the position vector of the center of the  $i$ th Gaussian function. The  $\sigma$  states were expanded with six Gaussians centered on each nucleus and one at the molecular midpoint. The exponents  $\alpha_i$  were those of the Schwartz seven-term wavefunction.<sup>5</sup> For Gaussians on the He nucleus in  $HeH^{2+}$  the  $\alpha_i$  were scaled by a factor of 4. The  $\pi$  wavefunctions were constructed from Whitten's Gaussian lobe  $2p$  functions,<sup>6</sup> but the linear coefficients were found from the molecular secular equation. As an indication of the accuracy obtainable from these simple wavefunctions we note that the energies were within 0.01 hartree of the exact energy for all states of  $H_2^+$  at all internuclear distances.

The usual formulas for the oscillator strength are

$$f(\mathbf{r}) = \frac{2}{3} G \Delta E | \langle \psi_i, \mathbf{r} \psi_j \rangle |^2, \quad (1)$$

and

$$f(\nabla) = \frac{2}{3} (G/\Delta E) | \langle \psi_i, \nabla \psi_j \rangle |^2. \quad (2)$$

$\Delta E$  is the transition energy in hartrees,  $G$  the degeneracy factor, and  $\psi_i$  and  $\psi_j$  the wavefunctions of the initial and final states.<sup>7</sup> For exact wavefunctions, or approximate wavefunctions under certain conditions,<sup>8</sup> we have,

$$\Delta E \langle \psi_i, \mathbf{r} \psi_j \rangle = \langle \psi_i, \nabla \psi_j \rangle. \quad (3)$$

From (1), (2), and (3) we obtain,

$$f(\mathbf{r}, \nabla) = (2G/3) | \langle \psi_i, \mathbf{r} \psi_j \rangle | | \langle \psi_i, \nabla \psi_j \rangle |. \quad (4)$$

While all these formulas are identical for exact wavefunctions they usually give quite different results with