Quantum-Mechanical Calculations for the Electric Field Gradients and other Electronic Properties of Lithium Hydride: The Use of Mixed Orbital Sets*

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We propose for quantum-mechanical calculations on diatomic molecules the use of mixed orbital sets composed of both Slater-type orbitals and elliptic orbitals. The Slater-type orbitals provide a good representation of the essentially spherical charge distributions near atoms in molecules and the elliptic orbitals provide good electronic distributions for the delocalized valence electrons. We have carried out calculations with up to 28 terms of the mixed orbital set on the lithium hydride molecule and obtained the most accurate wave function yet published. Our values for the several molecular parameters are as follows: (the experimental values are given in parenthesis)

$$-E = 8.0561 \text{ a.u.} (8.0703); R_e = 3.046 \text{ a.u.} (3.013);$$
$$\omega_e = 1438 \text{ cm}^{-1} (1406); \omega_e x_e = 86 \text{ cm}^{-1} (23);$$
$$\mu_0 = 5.93 (5.88); \mu_1 = 6.00 (5.99); \mu_2 = 6.05 (6.10); [\mu_e/(R_e \partial \mu/\partial R|_{R_e})] = 1.74 (1.8 \pm 0.3).$$

As is usually the case, our results are superior to self-consistent field calculations. We have calculated the electric field gradients at both nuclei. The quadrupole coupling for D in LiD was obtained using q_H and yielding $eq_D Q_D/h = 34.2$ kc/sec (33 ± 1 kc/sec). When q_{Li} is combined with the experimental quadrupole coupling constant we estimate $Q_{Li} = -4.3 \times 10^{-26}$ cm^2. This is considerably larger than the shell-model estimate and supports the proposal that for odd-proton nuclei nucleons external to a shell deform it.

INTRODUCTION

THERE are in use at present two general methods[1] for obtaining accurate wave functions for small diatomic molecules. The SCF-MO-CI method employs the self-consistent field orbitals to construct the configurations for many configuration wavefunction. The VB-CI method employs valence bond structures (configurations) as configurations in a many-configuration wave function. The relative merits of the two formulations have been discussed recently by the authors.[2] The second method is used in this paper.

Most previous calculations done heretofore by either method have been carried out using Slater-type orbitals.[1] Slater-type orbitals provide a good representation for the essentially spherical charge distributions near atoms in molecules but are not particularly suited for describing valence electrons. Another basis which has been less used[3-8] is the elliptic orbital basis [see Eq. (2)]. These functions are particularly well suited for describing the axially symmetric charge distributions associated with "bonding" or "valence" electrons while representation of the spherical atomic distributions in this basis is rather cumbersome. It occurred to

us that a wave function basis chosen appropriately from both Slater-type and elliptic orbitals would provide a more rapidly converging and conceptually satisfying description of a molecule than either taken separately.[9]

In this paper we present calculations on the lithium hydride molecule using wave functions of up to twenty-eight generalized valence bond configurations constructed from a mixed orbital set. On comparison of our computed molecular parameters with the observed ones (see Table I) we conclude that our wave function is considerably better than any heretofore published.

THE WAVE FUNCTION

The specification of an electronic wave function requires the specification of orbitals, orbital exponents, and electronic configurations. In our mixed basis set the Slater-type orbitals are defined by

$$\chi(n,l,m) = N(n,l) r^{n-1} e^{-\gamma r} Y_l{}^m(\theta, \phi)$$
$$= n a_m, \tag{1}$$

where $a = s, p, d, \cdots$ for $l = 0, 1, 2, \cdots$.

The elliptic[10] orbitals are of the form

$$\phi(n,l,m) = (-1)^{(|m|-m)/2} \lambda^n \mu^l [(\lambda^2-1)(1-\mu^2)]^{|m|/2}$$
$$\times e^{-\gamma\lambda - \beta\mu} e^{im\phi}. \tag{2}$$

[1] For a recent summary, see J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, 1963), Vol. I.

[2] J. C. Browne and F. A. Matsen, J. Phys. Chem. **66**, 2332 (1962).

[3] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).

[4] Many authors since James and Coolidge have used elliptic orbitals for H₂ calculations.

[5] J. K. Knipp, J. Chem. Phys. **4**, 300 (1936).

[6] F. T. Ormand and F. A. Matsen, J. Chem. Phys. **29**, 100 (1958).

[7] F. E. Harris, J. Chem. Phys. **32**, 3 (1960).

[8] H. M. James, J. Chem. Phys. **2**, 794 (1934).

[9] J. C. Browne and F. A. Matsen, Bull. Am. Phys. Soc. **8**, 123 (1963). Since the publication of this abstract we have learned that F. E. Harris and H. H. Michaels have planned similar calculations. References 5, 6, and 8 used 1s functions for core orbitals and a restricted class of elliptic orbitals for the valence electrons. None of them used configuration interaction in the core. It should be noted that the 1s orbital is a special case of the simplest elliptic orbital [see Eq. (2)]. These calculations can, in a strict sense, be considered as using a purely elliptic basis.

[10] See J. M. Miller, J. M. Gerhauser, and F. A. Matsen, *Quantum Chemistry Integrals and Tables* (University of Texas Press, Austin, 1959), p. 11, for definition of the elliptic coordinates. See also M. Kotani, A. Amemiya, E. Ishiguiro, and T. Kimura, *Tables of Molecular Integrals* (Maruzen Company, Ltd., Tokyo, 1955).

TABLE I. Summary of significant LiH calculations.

		This calc.	Experiment[a,b,c]	Ishiguro[d]	Hurst[e]	Karo[f]	Harris[g]	Ebbing[h]	Kahalas[i]	Browne[j]
$-E$	(a.u.)	8.0561	8.0703		7.9761		8.0397	8.04127	8.0171	8.04379
		$R=3.046^k$			$R=3.013$		$R=3.2$	$R=3.0$	$R=3.02$	$R=3.075$
D_e^{LB}	(eV)	2.12^l	2.516				1.404	1.725	1.067	1.793
D_e^R	(eV)	2.34^m	2.516	1.97		1.67	2.21			2.04
R_e	(a_0)	3.046	3.015	≈3.3		3.25				3.075
ω_e	(cm^{-1})	1438	1406	1130		1212				1602
$\omega_e X_e$	(cm^{-1})	86	23							28
$-\mu_0(R_0=3.069)$	(D)	5.93	5.88			6.04	6.05	5.96	5.89	5.57
$-\mu_1(R_1=3.11)$	(D)	6.00								
$-\mu_2(R_2=3.16)$	(D)	6.05								
$\mu_e/[R_e(\partial\mu/\partial R\,|_{R_e})]$		1.74	1.8±3				4.5	1.53		
$[(q/2e)_{Li}]$	(a_0^{-3})	−0.0173							−0.0166	
$[(q/2e)_{H}]$	(a_0^{-3})	−0.0258	0.249						0.0274	

a G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), 2nd ed., Table 39.
b R. Velasco, Can. J. Phys. **35**, 1024 (1957).
c See Ref. 14.
d E. Ishiguro, *Proceedings of Symposium on Molecular Physics* (Maruzen Company, Ltd., Tokyo, 1954), p. 10.
e R. P. Hurst, J. Miller, and F. A. Matsen, J. Chem. Phys. **26**, 1092 (1957).
f A. M. Karo and A. R. Olson, J. Chem. Phys. **30**, 1232 (1959).
g F. E. Harris and H. Taylor (unpublished).
h See Ref. 12.
i See Ref. 19.
j J. C. Browne and F. A. Matsen, J. Phys. Chem. **66**, 2332 (1962).
k R value in a_0 at which $-E$ was evaluated.
l $D_e^{LB} = E$(exp atoms) $-E$(calc, molecule), gives an absolute lower bound for D_e.
m $D_e^R = E$(calc, atoms) $-E$(calc, molecule).

Our largest wave function can be written

$$\Psi = \sum_{j=1}^{28} c_j \Psi_j , \qquad (3)$$

where

$$\Psi_j = \Psi_j(\chi_a \chi_b : \chi_c \chi_b)$$

or

$$\Psi_j(\chi_a \chi_b : \phi_c \phi_d)$$

and each Ψ_j has $^1\Sigma$ symmetry with orbital pairs separated by a colon. The twenty-eight coefficients together with the c_j for $R=3.0$ a.u. are listed in Table II. In each term the Li core electrons are represented by Slater-type orbitals and the valence electrons by elliptic orbitals. The terms numbered 16 and 23 in Table II couple core and valence electrons. The terms numbered 9, 11, and 28 allow for core polarization. The orbital exponents for the Slater-type orbitals making up the core configurations were taken from an eight-term calculation on the Li atom[11] which yielded an energy of -7.470 a.u. ($E_{exp} = -7.479$ a.u.). The orbital exponents for the elliptic orbitals were determined from a twelve-term (see Table III) calculation on the LiH molecule which employed only a $1s^2$ configuration for the Li core electrons. Each orbital exponent for the elliptic orbitals was separately optimized and then rescaled together at each of the seven internuclear distances considered. The core orbitals were rescaled in

the molecular wave function at $R=3.0a_0$. The final orbital exponents for $R=3.0a_0$ are listed in Table IV. The initial separation of the wave function into two parts greatly reduced the computer time necessary to select good exponents. The orbital exponents thus selected should be reasonably close to optimal. In fact, at $R=3.0a_0$ the virial theorem is satisfied to within less than 0.5%. For the computation of q_{Li} we found it expedient to use a twenty-four term wave function in which the $1S$ Li core orbitals are allowed to become elliptical orbitals. See Table V for this wave function.

Some caution must be observed in the selection of exponents in the elliptic orbitals with respect to possible occurrence of linear dependency and the positioning of nodes along the internuclear axis. Linear dependence among the prolate spheroidal (elliptic) basis proved, in fact, to be somewhat of a problem during the calculations.[12] Several terms which were considered had to be rejected because of linear dependence. The spread of the eigenvalues of the nonorthogonality matrix for the final twenty-eight term wave function was or order 10^5. The Control Data 1604 upon which these calculations were carried out carries roughly eleven decimal digits in floating point arithmetic and the energies proved to be quite stable under minor perturbations such as rearrangement of wave function terms and variation of the quadrature formulas for the two-electron two-center integrals.

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11 A single Slater-type $2s$ orbital was used for the outer electron.

12 See D. D. Ebbing, J. Chem. Phys. **36**, 1361 (1963); and P. O. Lowdin, Advan. Phys. **5**, 46 (1956) for discussion of the linear dependence problem.

TABLE II. Wave function, $\Psi = \sum_{j}^{28} c_j\Psi_j$.

j	Ψ_j	$c_j(R=3.0a_0)$
1	[1s1s: φ(0,0,0)φ(1,0,0)]	+0.13273
2	[1s1s: φ(0,0,0)φ(0,2,0)]	−0.08363
3	[1s1s: φ(0, 0, −1)φ(0,0,1)]	+0.16351
4	[1s1s: φ(1,1,0)φ(1,1,0)]	−0.01487
5	[1s'1s': φ(0,0,0)φ(1,0,0)]	+0.01489
6	[1s'2s: φ(0,0,0)φ(1,0,0)]	+0.02546
7	[2s2s: φ(0,0,0)φ(1,0,0)]	+0.00592
8	[2p₁2p₋₁: φ(0,0,0)φ(1,0,0)]	+0.00346
9	[2p₀2p₀: φ(0,0,0)φ(1,0,0)]	−0.00346
10	[3p₁3p₋₁: φ(0,0,0)φ(1,0,0)]	+0.00488
11	[3p₀3p₀: φ(0,0,0)φ(0,0,0)]	−0.00483
12	[(3d)²: φ(0,0,0)φ(0,0,0)]	−0.00060
13	[1s'1s': φ(0,0,0)φ(0,2,0)]	−0.01149
14	[1s'2s: φ(0,0,0)φ(0,2,0)]	−0.01509
15	[2s2s: φ(0,0,0)φ(0,2,0)]	−0.00947
16	[1s'φ(1,0,0): 2sφ(1,0,0)]	+0.00045
17	[1s1s: φ'(0,0,0)φ(0,0,0)]	+0.63647
18	[1s1s: φ(0,1,0)φ(0,0,0)]	−0.01078
19	[1s1s: φ(0,0,0)φ(2,0,0)]	−0.10785
20	[1s1s: φ(2,0,0)φ(2,0,0)]	+0.02191
21	[2p₁3p₋: φ(0,0,0)φ(1,0,0)]	−0.00227
22	[2p₀3p₀: φ(0,0,0)φ(1,0,0)]	+0.00226
23	[1s'φ'(0,0,0): 2sφ(1,0,0)]	−3.90687
24	[1s1s: φ(1,1,0)φ'(0,0,0)]	+0.12787
25	[1s1s: φ(1,0,0)φ'(0,0,0)]	−0.05389
26	[1s1s: φ(0,2,0)φ'(0,0,0)]	+0.12667
27	[1s1s: φ(0,1,0)φ'(0,0,0)]	+0.01019
28	[1s'2p₀': φ(0,0,0)φ(1,0,0)]	−0.00104

$E(R=3.0a_0) = -8.05603$ a.u.

TABLE IV. Orbital exponents at $R=3.0a_0$ for twenty-eight term wave function.

Orbital	Exponent	
1s	2.66	
1s'	4.13	
2s	2.62	
2p	5.17	
2p'	2.62	
3p	5.17	
3d	5.66	
φ(0,0,0)	1.75	−1.5
φ'(0,0,0)	2.75	−0.92
φ(1,0,0)	1.28	−0.50
φ(0,1,0)	0.88	−0.643
φ(0, 0, ±1)	1.9	−1.15
φ(1,1,0)	1.38	−1.31
φ(2,0,0)	2.45	−1.36
φ(0,2,0)	1.43	1.47

in column two for comparison. The error in the total energy of this calculation is less than one half the error in the best previous calculated energy. We note that the use of the mixed "natural" basis set allowed this improvement with little increase in the size of the basis. The R_e and E_e values for this calculation were obtained by a cubic fit of the computed points at $R=2.6a_0$, $3.0a_0$, $3.1a_0$, and $3.4a_0$. The calculated spectroscopic constants were obtained by fitting a fourth-order polynomial to five

TABLE V. The 24-term wave function with 1s² replaced by

$$\phi''^2(0,0,0) \quad \Psi = \sum_{j=1}^{24} c_j\Psi_j.$$

j	Ψ_j
1	[φ''(0,0,0)φ''(0,0,0): φ(0,0,0)φ(1,0,0)]
2	[φ''(0,0,0)φ''(0,0,0): φ(0,0,0)φ(0,2,0)]
3	[φ''(0,0,0)φ''(0,0,0): φ(0,0,1)φ(0, 0, −1)]
4	[φ''(0,0,0)φ''(0,0,0): φ(1,1,0)φ(1,1,0)]
5	[1s'1s': φ(0,0,0)φ(1,0,0)]
6	[1s'2s: φ(0,0,0)φ(1,0,0)]
7	[2s2s: φ(0,0,0)φ(1,0,0)]
8	[2p²(¹S₀): φ(0,0,0)φ(1,0,0)]
9	[3p²(¹S₀): φ(0,0,0)φ(1,0,0)]
10	[3d²(¹S₀): φ(0,0,0)φ(1,0,0)]
11	[1s'1s': φ(0,0,0)φ(0,2,0)]
12	[1s'2s: φ(0,0,0)φ(0,2,0)]
13	[2s2s: φ(0,0,0)φ(0,2,0)]
14	[φ''(0,0,0)φ''(0,0,0): φ(0,0,0)φ'(0,0,0)]
15	[φ''(0,0,0)φ''(0,0,0): φ(0,0,0)φ(0,1,0)]
16	[φ''(0,0,0)φ''(0,0,0): φ(0,0,0)φ(2,0,0)]
17	[φ''(0,0,0)φ''(0,0,0): φ(2,0,0)φ(2,0,0)]
18	[2p₊3p₋: φ(0,0,0)φ(1,0,0)]
19	[2p₀3p₀: φ(0,0,0)φ(1,0,0)]
20	[φ''(0,0,0)φ''(0,0,0): φ'(0,0,0)φ(1,1,0)]
21	[φ''(0,0,0)φ''(0,0,0): φ'(0,0,0)φ(1,0,0)]
22	[φ''(0,0,0)φ''(0,0,0): φ'(0,0,0)φ(0,2,0)]
23	[φ''(0,0,0)φ''(0,0,0): φ'(0,0,0)φ(0,1,0)]
24	[1s'φ'(0,0,0): 2sφ(0,0,0)]

RESULTS

Energy, Spectroscopic Constants, and Dipole Moment

In Table I are gathered together the principle results obtained in this calculation and from the significant earlier calculations. The experimental results are given

TABLE III. The twelve-term wave function $\Psi = \sum_{j=1}^{12} c_j\Psi_j$.

j	Ψ_j	$c_j(R=3.0a_0)$
1	[1s1s: φ(0,0,0)φ(1,0,0)]	0.192354
2	[1s1s: φ(0,0,0)φ(0,2,0)]	−0.127887
3	[1s1s: φ(0,0,0)φ(0,0,1)]	0.171317
4	[1s1s: φ(1,1,0)φ(1,1,0)]	−0.015470
5	[1s1s: φ(0,0,0)φ'(0,0,0)]	0.643884
6	[1s1s: φ'(0,0,0)φ'(0,0,0)]	−3.954195
7	[1s1s: φ(0,0,0)φ(2,0,0)]	−0.091389
8	[1s1s: φ'(0,0,0)φ(2,0,0)]	0.103586
9	[1s1s: φ'(0,0,0)φ(1,0,0)]	−0.057502
10	[1s1s: φ'(0,0,0)φ(0,2,0)]	0.134285
11	[1s1s: φ(0,0,0)φ(0,1,0)]	−0.016202
12	[1s1s: φ'(0,0,0)φ(0,1,0)]	0.015349

computed points. ω_e is given quite accurately but the higher members of the vibration series are given very poorly. The dipole moment in the lowest vibrational state and the dipole moment derivative at our equilibrium separation of $R_e = 3.046 a_0$ were obtained from a quadratic fit of the calculated dipole moment values at $R = 2.9 a_0$, $3.0 a_0$, and $3.1 a_0$. These values are in excellent agreement with the experimental values as can be seen from Table I.

We calculated the dipole moments for the higher vibrational states by evaluating the quadratic in the dipole moment mentioned previously at R_v, where

$$R_v = [(R_e)^2 (B_e / (B_e - \alpha_e(v + 1/2)))]^{1/2} - R_e + R_e(\text{calc.}).$$

Here experimental values were used for the spectroscopic constants except for $R_e(\text{calc})$. This adjustment was necessary since $R_e(\text{calc}) \neq R_e(\text{exp})$.

THE QUADRUPOLE MOMENT OF Li⁷ AND THE QUADRUPOLE COUPLING CONSTANT OF LiD

The most significant observable quantity resulting from the derivation of a nucleus in an atom or molecule from spherical symmetry is the quadrupole coupling constant,[13] eqQ/h. Now Q is the quadrupole moment of the nucleus and q is the electric field gradient due to the electronic environment of the nucleus. For atom A of a diatomic molecule

$$q_A = 2e\langle \Psi_{\text{el}} | P_2(\cos\theta_A)/r_A^3 | \Psi_{\text{el}} \rangle + 2eZ_B \langle \Psi_{\text{vib}} | R^{-3} | \Psi_{\text{vib}} \rangle$$
$$= (q_{\text{el}})_A + (q_{\text{nuc}})_A. \tag{4}$$

The quadrupole coupling constants for LiH and LiD were first measured in 1961 by Klemperer, Wharton, and Gold.[14] For LiH much interest is attached to obtaining Q_{Li}^7 via q_{Li} obtained through an electronic wave function since Q_{Li}^7 has not been otherwise measured. Since Q_D is fairly well established q_D obtained from an electronic wave function can be used to obtain an eqQ/h to compare with the experimental value, thus providing a useful comparison of the wave function to experiment.

In order to compute q_D from Eq. (4) we obtained a numerical Ψ_{vib} by numerically integrating the one-dimensional radial Schrödinger's equation using as a potential function a Hurlburt-Hirschfelder[15] potential function determined by our computed spectroscopic constants (for LiD). Using this Ψ_{vib} we find $(q_{\text{nuc}})_D = 0.0350 a_0^{-3}$. On combining this with $(q_{\text{el}})_D = -0.0776$ a_0^{-3} obtained from the twenty-eight wave functions of

Table II and the Q_D value given by Auffray[16] we find $(eqQ/h)_D = 34$ kc/sec, which is in very good agreement[17] with the experimental value of $(eqQ/h)_D = 33 \pm 1$ kc/sec. Earlier theoretical estimates of $(eqQ/h)_D$ have been made by Kolker and Karplus,[18] $(eqQ/h)_D = 35.5$ kc/sec using a relatively crude SCF-MO wave function and by Nesbet and Kahalas[18,20] $(eqQ/h)_D = 36.7$ kc/sec using a better SCF-MO wave function.

Historically, the first attempt to determine Q_{Li}^7 via a quadrupole coupling constant and Eq. (4) was by Harris and Melkanoff[21] in 1953 using the eqQ/h data of Kusch[22] for Li₂ and the James[23] Li₂ wave function. Unfortunately, for Li₂ $(q_{\text{el}})_{\text{Li}} \approx - (q_{\text{nuc}})_{\text{Li}}$ so that in this case several significant figures in both quantities are needed to obtain meaningful results for q_{Li}. Several authors[23,24] later tried to improve upon the inconclusive results obtained by Harris and Melkanoff for q_{Li} from Li₂. Nesbet and Kahalas[25] recognized, when eqQ/h for LiH became available[2] in 1961, that this molecule offered a better circumstance for obtaining an accurate q_{Li} since $(q_{\text{el}})_{\text{Li}}$ and $(q_{\text{nuc}})_{\text{Li}}$ are substantially different for LiH. In a later paper,[19] Kahalas and Nesbet report q_{Li} and Q_{Li} values obtained from SCF-MO wave functions using several different basis sets. They found that the addition of $3d\sigma_{\text{Li}}$ orbitals to the atomic orbital basis set for the SCF-MO calculations caused substantial changes in q_{Li}.

In the remainder of the section we discuss calculations leading to what we believe is the most accurate value yet found for Q_{Li}^7. It has been suggested[17,23] that the quadrupolar deviations from spherical symmetry of atomic cores in molecules can substantially influence $(q_{\text{el}})_A$ values. This distortion can result from two sources the polarization of the electronic charge distribution by the nuclear quadrupole,[26] and the distorting effect of the remainder of molecular charge distribution. Provision for the latter effect can readily be put in a molecular wave function by including terms which add quadrupolar character to the polarization of the atomic-like core. A careful scrutiny of Table II

[13] See C. H. Townes, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 38, for a review of experimental and theoretical results relating to nuclear quadrupole effects.

[14] L. Wharton, L. P. Gold, and W. Klemperer, J. Chem. Phys. **37**, 2149 (1962). Some of the results were first reported at the June 1961 Ohio State Symposium on Molecular Spectroscopy.

[15] H. M. Hurlburt and J. O. Hirschfelder, J. Chem. Phys. **9**, 6 (1941); **35**, 1901 (1961).

[16] J. P. Auffray, Phys. Rev. Letters **6**, 120 (1961). Auffray obtains Q_D by evaluating $(q_{\text{el}})_D$ from the Kolos-Roothaan D₂ wave function.

[17] Note that we have not considered the polarization of the electronic charge distribution by the nuclear quadrupole. See, for example, R. M. Sternheimer, Phys. Rev. **84**, 244 (1951); **86**, 316 (1952); or Ref. 23. Neither, however, was this effect considered by Auffray, Ref. 16 in his evaluation of Q_D.

[18] H. J. Kolker and M. Karplus, J. Chem. Phys. **36**, 960 (1962).

[19] S. L. Kahalas and R. K. Nesbet, J. Chem. Phys. **39**, 529 (1963).

[20] Kahalas and Nesbet used $Q_D = -2.73 \times 10^{-27}$ cm². We have converted their eqQ/h to $Q_D = -2.82 \times 10^{-27}$ cm² to facilitate comparison.

[21] E. G. Harris and M. A. Melkanoff, Phys. Rev. **90**, 585 (1953).

[22] R. H. Logan, R. E. Cote, and P. Kusch, Phys. Rev. **86**, 280 (1952).

[23] R. M. Sternheimer and H. M. Foley, Phys. Rev. **92**, 1460 (1953).

[24] I. Mannari and T. Arai, J. Chem. Phys. **28**, 28 (1958).

[25] S. L. Kahalas and R. K. Nesbet, Phys. Rev. Letters **6**, 549 (1961).

[26] See Ref. 17 for references on these matters. Also Ref. 13.

TABLE VI. Comparison of some expectation values. $R = 3.046a_0$.

	12-term function of Table III	28-term function of Table II	12-term function of Table III with $1s^2$ replaced by $\phi''^2(0,0,0)$	14-term function. See text for description	24-term function of Table V
E (a.u.)	−8.0051	−8.0561	−8.0060	−8.0051	−8.0565
μ_0(D)	−5.84	−5.911	−5.83	−5.85	−5.92
$(q_{el}/2e)_H a_0^{-3}$	−0.0754	−0.0776	−0.0752	−0.0754	−0.0777
$(q_{el}/2e)_{Li} a_0^{-3}$	−0.0550	−0.0555	−0.0500	−0.0534	−0.0521

reveals, however, that while there are a number of terms in the twenty-eight term wave function which allow for core polarization, none of them can add appreciable quadrupolar character to the Li core. Therefore, we constructed wave functions which give "core polarization" directly rather than in multipole components by replacing the $1s^2$ Li core by $\phi''^2(0,0,0)$ [see Eq. (2)] and selecting optimum values for γ and β. [Note that if $\gamma = \beta$, $\phi(0,0,0)$ differs from $1s_{Li}$ only by normalization.] Calculations of this type were carried out with the 12-term function of Table III and with a twenty-four term function obtained by deleting from the twenty-eight term function most other provision for "core polarization" (see Table V). In each case optimization of γ and β yielded a ratio $\gamma/\beta = 0.976$ indicating a slight shift of charge density out of the internuclear region. Then in order to provide a comparison of this means of adding quadrupolar core polarization to the direct multipole expansion we constructed a 14-term function by adding two terms involving $3d\sigma_{Li}$ orbitals in the Li core to the 12-term function and optimized the orbital exponent of the $3d\sigma_{Li}$ orbital. In Table VI we list the energies, μ_0, $(q_{el})_{Li}$, and $(q_{el})_H$ from these and certain other computations. These results can be summarized in a few sentences. The twenty-eight term and twenty-four term functions yield virtually identical values for energy, $(q_{el})_H$, and μ_0 but different $(q_{el})_{Li}$ values. These results imply (a) that both functions have closely similar charge distributions and almost the same allowance for the energy due to "core polarization"; (b) that they differ in the amount of quadrupolar character in the distortion of the core. We further note that the twenty-eight term function gives virtually the same $(q_{el})_{Li}$ as the 12-term function which has a totally spherically symmetrical core. The 12-term function with the elliptic core gives a larger change in $(q_{el})_{Li}$ than the 14-term function with the $3d\sigma$ terms in the Li core but in the same direction. This indicates that the use of elliptic core orbitals is an effective way of introducing the quadrupolar core distortion into the wave function. Furthermore, obtaining similar values by different means adds substance to the values. We have, therefore, used the $(q_{el})_{Li}$ from the twenty-four term function in computing $(q_{total})_{Li}$. Computing a Ψ_{vib} as previously described and

using the numerical Ψ_{vib} in Eq. (4) we find $(q_{nuc})_{Li} = 0.0348a_0^{-3}$. This gives $(q_{total}/2e) = 0.0173a_0^{-3}$. Since $eqQ/h = 346$ kc/sec, we find $(Q_{Li}/e) = -4.3 \times 10^{-26}$ cm². This is in agreement with those results of Kahalas and Nesbet[18] which they regard as most reliable, $(q_{total}/2e) = -0.0166a_0^{-3}$ and $(Q_{Li}/e) = -4.44 \times 10^{-26}$ cm². It should be noted, however, that Kahalas and Nesbet set $q_{nuc} = 2ZR_e^{-3}$ rather than computing the expectation value. Including this factor in their calculations would make their value for Q_{Li}/e less negative, probably bringing it closer to the results reported here. Our discussion also explains the change in $(q_{el})_{Li}$ found by Kahalas and Nesbet upon the addition of $3d\sigma_{Li}$ orbitals to their SCF-MO basis.

There are no direct experimental determinations of (Q/e) for Li⁷. The only alternate values are those obtained from $(1p)^3$ configurations of the shell model nucleus.[27] From $Q/(e\langle r^2 \rangle) = (2J - 2Z + 1)/2(J + 1)$ and $J = \frac{3}{2}$ one obtains $Q/(e\langle r^2 \rangle) = -0.20$. A more recent estimate[28] gives $Q/(e\langle r^2 \rangle) = -0.25$. If one takes $\langle r^2 \rangle^{1/2} = 1.5 \times 10^{-3} A^{1/3}$ cm there is obtained $\langle r^2 \rangle = 8.24 \times 10^{-26}$ cm², which gives $Q/e = -2.06 \times 10^{-26}$ cm². Van der Merwe[28] prefers for $1p$ nucleons $\langle r^2 \rangle < 10^{-25}$ so that $|Q/e| < 2.5 \times 10^{-26}$ cm². Thus the shell model value is considerably smaller than that obtained from the experimentally obtained coupling constant and the theoretical electronic q. This is not unusual for nuclei of odd Z.[29] It has been postulated that the nucleons outside a closed shell deform the surface of a shell.

A recent estimate[28] of the quadrupole moment taking these deformations into account yields $Q/2(e\langle r^2 \rangle) = -3/5$ or $|Q/e| < -6.0 \times 10^{-26}$ cm². It is seen that the quadrupole moment obtained from the experimentally determined quadrupole coupling constant and the theoretically determined electric field gradient is bracketed by the values obtained from the simple nuclear shell model and the simple nuclear shell model with surface coupling and is presumably more accurate than either.

[27] R. G. Sachs, Nuclear Theory (Addison-Wesley Publishing Company, Reading Massachusetts, 1953), p. 259.
[28] J. H. van der Merwe, Phys. Rev. 131, 2181 (1963).
[29] J. Rainwater, Phys. Rev. 79, 432 (1950); A. Bohr and B. R. Mottelson, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. 28 (1959).

THE RELATIONSHIP BETWEEN THE FORCE CONSTANT AND THE ELECTRIC FIELD GRADIENTS

It has been shown[30] that the Hellman-Feynman theorem leads to the following relationship

$$\Delta_A = k/Z_A - q_A = (4\pi/3)\rho(A) - \int \partial\rho/\partial X_A \, \cos\theta_A/r^2 A d\tau.$$

Here k is the force constant, q_A is the electric field

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[30] L. Salem, J. Chem. Phys. 38, 1227 (1963).

gradient at nucleus A, $\rho(A)$ is the electron density at nucleus A and X_A is the nuclear position coordinate. We find from our computed values of q_A and $\rho(A)$ at $R=3.0a_0$ that $\Delta_{\text{Li}}=+0.063a_0^{-3}$ and $\Delta_{\text{H}}=+0.0043a_0^{-3}$.

It can be shown[30] that $\Delta_A = 0$ if the charge distribution around A is spherical and if it follows the motion of A. Inspection of the LiH wave function shows that these conditions are not met and that small value of Δ_{H} is due to a fortuitous cancellation of $\rho(A)$ and $\int(\partial\rho/\partial X_A)$ $\times (\cos\theta_A/r^2)d\tau$. When q_A is negative as for lithium, the cancellation clearly cannot occur.

Single-Quantum Annihilation of Positrons*

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Calculations of the cross section for single-quantum annihilation of positrons by K-shell electrons in the Coulomb field of a nucleus are presented. Numerical results are given for nuclear charges $Z=73, 74, 78, 79, 82,$ and 90 and for energies from threshold to 1.75 MeV. For $Z=82$ the numerical results agree well but not in detail with previous results of Jaeger and Hulme, and show that the Born approximation is too large by a factor of nearly 2.

I. INTRODUCTION

THERE has been some recent experimental interest in the process of single-quantum annihilation of positrons.[1] In a one-photon process recoil momentum must be taken up by a nucleus, so that annihilation is more probable in the K shell than in outer atomic shells. The K-shell annihilation cross section is known numerically for lead, $Z=82$, from the computation of Jaeger and Hulme[2]; and analytically for arbitrary Z from the Born approximation.[3]

The Born-approximation formula, Eq. (20), shows that the cross section is proportional to Z^5; annihilation is therefore more probable for heavy elements than for light. For elements with Z greater than 70 the Born parameter αZ is greater than $\frac{1}{2}$ and the Born approximation is certainly not reliable.

Because of the need for accurate cross sections for elements other than lead it was decided to formulate the problem in such a way that a detailed numerical analysis would be simple.

In Sec. II we explain how the single-photon cross section is reduced to a sum of partial-wave cross sections corresponding to an angular momentum decomposition

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[1] L. Sodickson, W. Bowman, J. Stephenson, and R. Weinstein, Phys. Rev. 124, 1851 (1961).

[2] J. C. Jaeger and H. R. Hulme, Proc. Cambridge Phil. Soc. 32, 158 (1936).

[3] H. J. Bhabha and H. R. Hulme, Proc. Roy. Soc. (London) A146, 723 (1934).

of the incident positron wave function. The radial integrals occurring in the partial-wave cross sections are reduced to sums of hypergeometric functions in Sec. III. The results of the numerical analysis, together with a discussion of various limiting cases, are presented in Sec. IV.

The numerical results are in precise agreement with the Born approximation as $Z \to 0$, and agree approximately, but not in detail, with the results of Jaeger and Hulme for $Z=82$.

II. REDUCTION OF THE CROSS SECTION

The cross section for single-quantum annihilation is given by

$$\sigma = \frac{\alpha}{4\pi} \frac{W\omega}{p} \int d\Omega_{\text{k}} \sum_{\zeta,\epsilon,\mu} |M|^2, \tag{1}$$

where the matrix element M is

$$M = -i \int d^3r (v_\zeta^\dagger(\mathbf{r})\boldsymbol{\alpha} \cdot \hat{\epsilon} u_\mu(\mathbf{r})) e^{-i\mathbf{k}\cdot\mathbf{r}}. \tag{2}$$

In the above we denote the energy-momentum vectors of the positron and photon by $(\mathbf{p}, iW)$ and $(\mathbf{k}, i\omega)$; and the photon polarization vector by $\hat{\epsilon}$. The electron binding energy is given by $m\gamma_1$, where m is the electron mass and $\gamma_1 = (1-\alpha^2 Z^2)^{1/2}$. We use $v_\zeta(\mathbf{r})$ and $u_\mu(\mathbf{r})$ for the Coulomb field Dirac wave functions of a positron with spin ζ, and a K shell electron with magnetic quantum number μ, respectively.