



All Faculty Publications

1968-11-01

Expectation Values of Simple Correlated Helium-Atom Wavefunctions

Thomas P. Tsien

Russell T. Pack

Follow this and additional works at: <https://scholarsarchive.byu.edu/facpub>

 Part of the [Biochemistry Commons](#), and the [Chemistry Commons](#)

Original Publication Citation

Tsien, Thomas P. and Russell T. Pack. "Expectation Values of Simple Correlated Helium-Atom Wavefunctions." *The Journal of Chemical Physics* 49 (1968): 4247-4248.

BYU ScholarsArchive Citation

Tsien, Thomas P. and Pack, Russell T., "Expectation Values of Simple Correlated Helium-Atom Wavefunctions" (1968). *All Faculty Publications*. 802.

<https://scholarsarchive.byu.edu/facpub/802>

This Peer-Reviewed Article is brought to you for free and open access by BYU ScholarsArchive. It has been accepted for inclusion in All Faculty Publications by an authorized administrator of BYU ScholarsArchive. For more information, please contact scholarsarchive@byu.edu, ellen_amatangelo@byu.edu.

The absorption spectra of the two anthraquinones show three maxima ($\pi\text{-}\pi^*$) at about 40 kK (I), 37 kK (II), and 31 kK (III), and a weak maximum ($n\text{-}\pi^*$) at 24 kK (IV). Transition I and II are not well resolved, and an additional transition begins to appear at lower energy. The phosphorescence spectra contain the (0, 0) bands designated A and three distinct vibrational-electronic bands B, C, and D. The polarization of the emission spectrum relative to the absorption is shown in Fig. 1 for 9,10-anthraquinone. The relative polarizations for 2-methyl-9,10-anthraquinone are similar. The emission bands A, B, C, and D all show the same polarization. The polarization of band I is not as pronounced as the others due to overlap with band II and the appearance of an additional band at higher energies or a vibronic progression of opposite polarization. Transition II definitely is polarized parallel to the triplet emission.

The lowest triplet observed in the single crystal spectrum of 9,10-anthraquinone⁶ has been related to that of benzoquinone⁷ and assigned the symmetry 3A_u . First-order perturbation theory involving spin-orbit coupling⁸ indicates the polarization of the transition ${}^3A_u \rightarrow {}^1A_g$ should be along the Z axis. The polarizations of the singlet transitions I, II, III, and IV are inferred to be Y, Z, Y, and Y, respectively, which agrees with the assignment of Drott and Dearman.

The emission bands B, C, and D which involve vibrational modes superimposed on the (0, 0) transition appear to be a simple multiple of a single vibrational frequency. The separation is approximately 1620 cm^{-1} in 9,10-anthraquinone and 1650 cm^{-1} in 2-methyl-9,10-anthraquinone. The frequencies do not differ greatly from the infrared-allowed carbonyl stretching modes of 1676 cm^{-1} in 9,10-anthraquinone (b_{1u})⁹ and 1670 cm^{-1} in 2-methyl-9,10-anthraquinone; however, in the first-order approximation, coupling of the (0, 0) band to an infrared-allowed transition leads to a symmetry-forbidden transition. Since the carbonyl vibration is expected to be important in the $n\text{-}\pi^*$ transition, we suggest that the Raman-active symmetric carbonyl stretch (a_{1g}) is involved although we have seen none in the 1700-cm^{-1} region.

The phosphorescence quantum yields for 9,10-anthraquinone and 2-methyl-9,10-anthraquinone are 0.50 and 0.55, respectively. The quantum yields were determined at 77°K and at concentrations of 6.43×10^{-4} and $6.64 \times 10^{-4} M$, respectively. The nonradiative decay processes which account for approximately 50% of the quanta absorbed are now being studied.

* We acknowledge the support of the Robert A. Welch Foundation and the T.C.U. Research Foundation.

¹ H. R. Drott and H. H. Dearman, *J. Chem. Phys.* **47**, 1896 (1967).

² A. C. Albrecht, *J. Mol. Spectry.* **6**, 84 (1961).

³ T. Azumi and S. P. McGlynn, *J. Chem. Phys.* **37**, 2613 (1962).

⁴ W. H. Melhuish, *J. Opt. Soc.* **52**, 1256 (1956).

⁵ H. V. Drushel, A. L. Sommers, and R. C. Cox, *Anal. Chem.* **35**, 2166 (1963).

⁶ H. H. Dearman, N. Sundarachari, and D. Ulka, *J. Chem. Phys.* **45**, 4363 (1966).

⁷ J. M. Hollas and L. Goodman, *J. Chem. Phys.* **43**, 760 (1965).

⁸ D. S. McClure, *J. Chem. Phys.* **17**, 665 (1949).

⁹ C. Pecile and B. Lunelli, *J. Chem. Phys.* **46**, 2109 (1967).

Expectation Values of Simple Correlated Helium-Atom Wavefunctions*

THOMAS P. TSIEN AND RUSSELL T. PACK

*Department of Chemistry, Brigham Young University,
Provo, Utah 84601*

(Received 17 May 1968)

In this Note we present the results of a calculation of the expectation values of a number of one- and two-electron properties of the ground-state helium atom using two very simple correlated wavefunctions.

It is well known¹ that the expectation values of one-electron properties calculated using Hartree-Fock or "best-orbital" wavefunctions are quite good, but that those of two-electron properties are quite poor, due to the inability of an orbital-type wavefunction to properly account for electron correlations. It has been suggested² that this deficiency be remedied by multiplying the orbital wavefunction by a "correlation factor" explicitly depending on the interelectronic distances, and it has been shown³ that even a very simple correlation factor produces a large improvement in the calculated energy. One expects a similar improvement in the calculated values of other two-electron properties, but few calculations have been done to demonstrate it.

To see just how much improvement a simple correlation factor would make in properties other than the energy and also to compare two different correlation factors, we calculated the expectation values of a number of properties of the ground-state helium atom using the two simple functions,

$$\psi_{\text{exp}} = \exp[-\zeta(r_1 + r_2)] \exp(\gamma r_{12}) \quad (1)$$

and

$$\psi_{\text{lin}} = \exp[-\zeta(r_1 + r_2)] (1 + \gamma r_{12}). \quad (2)$$

Here, r_1 and r_2 are the distances of the electrons from the nucleus, and r_{12} is the interelectronic distance. Both functions were first suggested by Hylleraas,⁴ and the parameters ζ and γ giving the best energies have been determined by several authors.^{3,4} There are indications⁵ that ψ_{exp} should be the better wavefunction, but ψ_{lin} gives a better energy, and its generalization to systems of more than two electrons leads to more tractable integrals. Bangudu and Robinson⁶ have calculated several expectation values using ψ_{exp} , but only the energy seems to have been calculated using ψ_{lin} .

In this work the values of the parameters were redetermined to give the lowest energy, and then these values of the parameters were used in the calculation of the other expectation values. The results are listed in

TABLE I. Expectation values (atomic units) of properties of the ground-state helium atom given by different approximate wavefunctions.

Operator	$\psi_{\text{hydrogenic}}$	ψ_{exp}	ψ_{lin}	Accurate (Pekeris) ^a	Hartree-Fock
ζ	1.6875	1.8581	1.8497		
γ	0	0.2547	0.3658		
$-E$	2.847656	2.889618	2.891121	2.903724	2.86168 ^b
r_1^2	1.0535	1.0972	1.0768	1.1935	1.1848 ^c
r_1	0.8889	0.9023	0.8968	0.9295	0.9273 ^c
$1/r_1$	1.6875	1.6892	1.6891	1.6883	1.6874 ^c
$1/r_1^2$	5.6953	5.8399	5.8136	6.0174	5.996 ^c
r_{12}^2	2.1070	2.3964	2.3273	2.5164	
r_{12}	1.2963	1.3858	1.3724	1.4221	1.362 ^d
$1/r_{12}$	1.0547	0.9774	0.9743	0.9458	1.026 ^d
$1/r_{12}^2$	1.8984	1.5944	1.5527	1.4648	
$1/r_1 r_2$	2.8477	2.8044	2.7871	2.7087	2.85 ^{d,e}
$1/r_1 r_{12}$	2.1357	2.0072	1.9859	1.9209	
$\delta(\mathbf{r}_1)$	1.5296	1.6587	1.6410	1.8104	1.795 ^{d,e}
$\delta(\mathbf{r}_{12})$	0.1912	0.1332	0.1199	0.1063	0.188 ^d
$\mathbf{p}_1 \cdot \mathbf{p}_2$	0	0.2490	0.2332	0.1591	0

^a Reference 7.^b Reference 3.^c S. Fraga and G. Malli, University of Alberta Division of Theoretical

Chemistry Rept. TC-6601, 1966.

^d P. Jennings and E. B. Wilson, Jr., J. Chem. Phys. **47**, 2130 (1967).^e Reference 1.

Table I and compared with results using a product of scaled hydrogenic orbitals,

$$\psi_{\text{hydrogenic}} = \exp[-\zeta(r_1 + r_2)], \quad (3)$$

which is the uncorrelated counterpart of our two correlated wavefunctions. Also listed for comparison are the expectation values given by Pekeris' exceedingly accurate 1048-term wavefunction⁷ and the Hartree-Fock approximation. All quantities are in Hartree atomic units.

The results in Table I allow one to make the following observations: (1) The correlation factors produce only very slight improvement in the values of the one-electron properties; (2) the correlation factors produce a large improvement in all the two-electron properties, and although the values of these properties given by such simple correlated wavefunctions are not accurate enough to be fully satisfactory, they are much better than those given by even the best orbital wavefunction; (3) the linear and exponential correlation factors give very similar results, and neither shows any distinct superiority; this is because the two correlation factors are very similar in the region of strong correlation (small r_{12}).

* Research supported in part by a grant from the Brigham Young University Research Fund.

¹ M. Cohen and A. Dalgarno, Proc. Phys. Soc. (London) **77**, 748 (1961).

² P.-O. Löwdin, Advan. Chem. Phys. **2**, 207 (1959), and references therein.

³ C. C. J. Roothaan and A. W. Weiss, Rev. Mod. Phys. **32**, 194 (1960), and references therein.

⁴ E. A. Hylleraas, Z. Physik **54**, 347 (1929).

⁵ L. C. Green, C. Stephens, E. K. Kolchin, C. C. Chen, P. R. Rush, and C. W. Ufford, J. Chem. Phys. **30**, 1061 (1959).

⁶ E. A. Bangudu and P. D. Robinson, Proc. Phys. Soc. (London) **86**, 1259 (1965).

⁷ C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

Low-Temperature Circular Dichroism of Hexahelicene*

O. E. WEIGANG, JR., AND P. A. TROUARD DODSON

Richardson Chemical Laboratories, Department of Chemistry,
Tulane University, New Orleans, Louisiana 70118

(Received 13 May 1968)

The circular dichroism of (+)-hexahelicene from 420 to 210 μ at 78°K has been obtained in PM (5:1 isopentane, methylcyclohexane) as well as EPA (5:5:2 ethyl ether, isopentane, ethanol) glasses. Parallel determinations of the fluorescence and absorption under the same conditions have established a number of important points concerning the various spectra.

Circular dichroism measurements were made using a Cary 60 recording spectropolarimeter with 6001 CD attachment. Low-temperature absorptions were obtained as described previously.¹ High-resolution fluorescence spectra were obtained with a Beckman DK-1A recording spectrophotometer with the lamp housing modified to receive an optical Dewar containing the sample. The housing optics collected the emission excited by a 200-W xenon arc with a $\text{KCr}(\text{SO}_4)_2$ solution filter. Hg line emissions were used throughout for wavelength calibration.

Figure 1 shows the hexahelicene absorption and