High-Order Perturbation Theory for a One-Electron Ion in a Uniform Electric Field*

Lawrence B. Mendelsohn

Department of Physics, Polytechnic Institute of Brooklyn, Brooklyn, New York 11201

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Large-Z expansion theory is applied to the nonrelativistic ground state of a one-electron ion and the subsequent first-order differential equations are solved recursively. For each order of perturbation theory, a general expression for the wave function is found. The substitution of this form into the perturbation-theory equations reduces the problem for the Kth-order wave function and energy to solving recursively a set of linear algebraic equations of approximately $2K$th order for the coefficients of certain radial polynomial terms appearing in the wave function. The asymptotic-series results for both the energy and the wave function are obtained explicitly through tenth order. For hydrogen a calculation of the ionization field (ignoring tunneling) gives a value of 3.36×10^8 V/cm. This agrees well with experimental results on field ionization and a recent accurate variational treatment and is found to be much superior to a WKB result.

INTRODUCTION

The problem we are considering is that of a one-electron ion in a uniform electric field. The field is assumed to be greater than 1000 V/cm so that the fine structure effects can be neglected in comparison with the perturbation effect of the electric field. Since the unit of electric field in atomic physics is 5.142×10^9 V/cm, a perturbation treatment is reasonable even for values of the electric field near the ionization field, Previous perturbation-theory calculations have transformed the Schrödinger equation to parabolic coordinates and then solved the two resulting second-order linear ordinary differential equations through either second order[1,2] or third order[3] in the field strength. Results up to second order in the ground-state wave function expressed in terms of spherical coordinates can also be found.[4,5] In the present paper, we apply the method of large-Z asymptotic expansions[6,7] to the calculation of the ground state using spherical coordinates. Using this technique the recursive equations to be solved are first order. Repeated solution of these equations leads to the appearance of $\ln r$ terms, where r is the radial distance of the electron from the nucleus. For the perturbation theory solution to be valid near the origin, the coefficients of the log terms must be set equal to zero. In so doing both the energy and the perturbation theory wave function are determined. Results obtained explicitly through third order indicate that the wave function corresponding to any arbitrary order assumes the form of a certain sum of products of Legendre polynomials and radial functions. These radial functions are themselves truncated polynomials in r. Assuming this form for the wave function, and substituting directly into the perturbation theory partial differential equations, the problem in any order N reduces to solving sets of linear algebraic equations recursively for the coefficients of the various powers of r in the radial functions and the energy in the Nth order. A general algebraic equation for any order is obtained [Eq. (27)] and results are calculated explicitly through tenth order on the IBM 360 computer. For hydrogen a calculation of the ionization field (ignoring tunneling) is made. The method developed here for one-electron problems appears to be a general one for obtaining perturbation theory results to arbitrarily high order.[7,8]

Before beginning our formal treatment it should be kept in mind that when a nonzero electric field is turned on, the discrete bound-state spectrum of the hydrogen atom goes over to packets of continuous energy states since the electron can tunnel through the potential barrier. Thus in the usual sense, no discrete energy levels exist for the perturbed problem – however observation of the Stark effect through spectroscope certainly indicates the existence of a perturbed bound states. This apparent anomaly has been resolved by Titchmarsh,[9] who has examined the Green's function for the one-dimensional analog Stark-effect problem and calculated the perturbed pole to first order in the field, and has shown that it agrees with the formal first-order perturbation theory result. Presumably this agreement can be extended to higher orders and three dimensions.[10] Since the spectral density is closely related to the size of the Green's function, it follows that the spectrum will be dense in the neighborhood of the pole, which corresponds to physical observation. However, it should not be surprising that our perturbation theory solutions turn out to be asymptotic and nonconvergent. This is of course no handicap since only a few terms give very accurate results.

II. THE BASIC ASYMPTOTIC EXPANSION

The Schrödinger equation of a one-electron ion with a nucleus of charge Z in a uniform electric field λ [$\lambda = \mathscr{E}/(5.142 \times 10^9$ V/cm$)$] can be written in the dimensionless form

$$-\tfrac{1}{2}(\partial^2\psi/\partial s^2) - s^{-1}(\partial\psi/\partial s) + (1/2s^2)L^2\psi - (Z/s)\psi - \lambda s \cos\theta \, \psi = E\psi \ , \tag{1}$$

where E is the energy of the system in atomic units (approximately 27.2 eV), s is the radial distance of the electron from the nucleus expressed in Bohr radii, and L^2 is the usual angular momentum operator. In the usual perturbation theory treatment, we make a transformation of variables $\xi = Zs$ and Eq. (1) becomes for $\Psi(\xi, \theta, \phi)$

$$-\tfrac{1}{2}(\partial^2\Psi/\partial\xi^2) - \xi^{-1}(\partial\Psi/\partial\xi) + (1/2\xi^2)L^2\Psi - \Psi/\xi - \epsilon\xi\cos\theta\,\Psi = (E/Z^2)\Psi , \qquad (2)$$

where $\epsilon = \lambda/Z^3$ is the natural perturbation theory parameter for the problem. Since there is no azimuthal angle dependence for S states, and the ground state is nondegenerate (no permanent dipole moment), we look for perturbation theory expansions

$$\text{(a)} \quad \Psi = \sum_{k=0}^{\infty} \epsilon^k \Psi_k(\xi, \theta) = e^{-\xi}\sum_{k=0}^{\infty}\epsilon^k b_k(\xi, \theta) , \quad \text{and (b)} \quad \frac{E}{Z^2} = -\sum_{m=0}^{\infty}\epsilon^{2m}E_{2m} , \qquad (3)$$

with $b_0 = 1$ and $E_0 = \tfrac{1}{2}$. We shall now return to Eq. (1) and obtain the basic asymptotic expansion which will then allow us to determine a general form for the b_k.

To obtain the basic asymptotic expansion we assume the form

$$\psi = e^{-Zh(s)}\sum_{j=0}^{\infty} a_j(s, \theta)Z^{-j} \qquad (4)$$

and substituting Eq. (4) and Eq. (3b) into Eq. (1) we obtain

$$-\frac{1}{2}\sum_{j=0}^{\infty}\left\{\left(\frac{dh}{ds}\right)^2 a_j Z^{-j+2} - \left(2\frac{dh}{ds}\frac{\partial a_j}{\partial s} + \frac{d^2h}{ds^2}a_j\right)Z^{-j+1} + \frac{2}{s}\left(1 - \frac{dh}{ds}\right)a_j Z^{-j+1}\right.$$

$$\left. + \left[\frac{\partial^2 a_j}{\partial s^2} + \frac{1}{s^2}\left(\cot\theta\frac{\partial a_j}{\partial\theta} + \frac{\partial^2 a_j}{\partial\theta^2}\right)\right]Z^{-j}\right\} - \sum_{j=0}^{\infty}s^{-1}\frac{\partial a_j}{\partial s}Z^{-j} - \lambda s\cos\theta\sum_{j=0}^{\infty}a_j Z^{-j} = -Z^2\sum_{s=0}^{\infty}\epsilon^{2s}E_{2s}\sum_{j=0}^{\infty}a_j Z^{-j} \qquad (5)$$

Setting the coefficients of the Z^2 and Z terms equal to zero successively, we obtain

$$h(s) = s \qquad (6)$$

and $a_0 = 1$. $\qquad (7)$

Continuing in this way, the recursion relation between any a_{j+1} and earlier coefficients in the expansion can be written

$$a_{j+1} = \int ds\left\{\frac{1}{2}\frac{\partial^2 a_j}{\partial s^2} + \frac{1}{s}\frac{\partial a_j}{\partial s} + \frac{1}{2s^2}\left[\left(\frac{\cos\theta}{\sin\theta}\right)\frac{\partial a_j}{\partial\theta} + \frac{\partial^2 a_j}{\partial\theta^2}\right] + \lambda\cos\theta\,sa_j - \sum_{r=1}^{\infty}{}_0\lambda^{1+r}E_{1+r}\sum_{k=0}^{j-(1+3r)}a_k\delta_{1,j-k-3r}\right\}, \qquad (8)$$

where the subscript 0 on the r sum indicates a sum only over odd values of r. We have assumed that no contributions come from the homogeneous solutions of the equation for a_{j+1}. Solving Eq. (8) recursively we find

$$a_1 = \lambda\cos\theta\,s^2/2 , \qquad (9)$$

$$a_2 = \lambda\cos\theta\,s + \lambda^2\cos^2\theta\,s^4/(2\times 4), \qquad (10)$$

$$a_3 = \lambda^2 s^3\left(\tfrac{15}{24}\cos^2\theta + \tfrac{1}{24}\right) + \lambda^3\cos^3\theta\,s^6/(2\times 4\times 6) \qquad (11)$$

$$a_4 = \lambda^2 s^2\left(\tfrac{45}{48}\cos^2\theta + \tfrac{21}{48}\right) + \lambda^3 s^5\left(\tfrac{9}{48}\cos^3\theta + \tfrac{1}{48}\cos\theta\right) + (\lambda^4 s^8\cos^4\theta)/(2\times 4\times 6\times 8), \qquad (12)$$

and $a_5 = \lambda^2(E_2 - \tfrac{9}{4})s + (\lambda^3 s^4/96)(31\cos\theta + 63\cos^3\theta) + (\lambda^4 s^7/192)(\cos^2\theta + 6\cos^4\theta) + \lambda^5\cos^5\theta\,s^{10}/(2\times 4\times 6\times 8\times 10)$. $\qquad (13)$

We note that if the coefficient of the s term in a_5 is not equal to zero, the evaluation of $(1/s)(\partial a_5/\partial s)$ would lead to a $\lambda^2 \ln s$ term in a_6. Since we have shown[7] for nonsingular problems, such as the one under consideration, that the basic asymptotic expansion is simply a reordering of terms of the perturbation theory expansion (terms with a larger $s(\xi)$ power in a given order of the perturbation series enter the basic asymptotic solution in a lower-order term), and we know that the perturbation theory expansion must be well behaved in the neighborhood of the origin, it follows that such $\ln s$ terms cannot appear in our expansion. Thus the coefficient must be zero giving us the well known result

$$E_2 = \tfrac{9}{4}. \tag{14}$$

Also since λ^2 terms will no longer appear in higher-order a_j, re-expressing ψ obtained thus far in terms of ξ should give us the correct perturbation theory expansion through second order plus some additional higher-order terms. In doing this we can also rewrite the $\sin\theta$ and $\cos\theta$ terms in terms of Legendre polynomials $Y_{l,0}(\theta)$ obtaining,

$$\psi = e^{-\xi}\{1 + \epsilon(\xi + \tfrac{1}{2}\xi^2)Y_{1,0} + (\epsilon^2/24)[(18\xi^2 + 6\xi^3 + \xi^4)Y_{0,0} + (15\xi^2 + 10\xi^3 + 2\xi^4)Y_{2,0}] + \theta(\epsilon^3)\}. \tag{15}$$

Continuing in the same manner we obtain

$$b_3 = Y_{1,0}\left(\tfrac{53}{8}\xi + \tfrac{53}{16}\xi^2 + \tfrac{71}{40}\xi^3 + \tfrac{43}{60}\xi^4 + \tfrac{2}{15}\xi^5 + \tfrac{1}{80}\xi^6\right) + Y_{3,0}\left(\tfrac{7}{20}\xi^3 + \tfrac{21}{80}\xi^4 + \tfrac{3}{40}\xi^5 + \tfrac{1}{120}\xi^6\right), \tag{16}$$

and $E_4 = 3555/64$. $\tag{17}$

As we go to higher orders such calculations become quite tedious. However the general form of the b_k for a well behaved solution now becomes apparent. That is we take

$$b_k = \sum_l^k Y_{l,0}(\theta)\sum_{j_l}^{2k} j B(k,l,j)\xi^j, \tag{18}$$

where the sum over l is odd or even as k is odd or even (beginning with $l = 1, 0$ respectively), $j_l = l$ for $l \neq 0$, $j_l = 2$ for $l = 0$, and the $B(k,l,j)$ are constants.

III. THE PERTURBATION THEORY SOLUTION

Substituting Eq. (3a) and Eq. (3b) into Eq. (2) the equation for b_k becomes

$$-\frac{1}{2}\frac{\partial^2 b_k}{\partial \xi^2} + \left(1 - \frac{1}{\xi}\right)\frac{\partial b_k}{\partial \xi} + \frac{1}{2\xi^2}L^2 b_k - \xi Y_{1,0} b_{k-1} + \sum_{m=1}^{(k/2)\mathrm{int}} E_{2m}b_{k-2m} = 0, \tag{19}$$

where $(k/2)_{\mathrm{int}}$ is the largest integer less than or equal to $k/2$. Now let us substitute Eq. (18) into the above. The first three terms in the above equation give

$$\sum_l Y_{l,0}\left(\sum_{j_l-1}^{2k-1}(j+1)B(k,l,j+1)\xi^j + \sum_{j_l-2}^{2k-2}A(l,j)B(k,l,2+j)\xi^j\right), \tag{20}$$

where $A(l,j) = -j^2/2 - 5j/2 - 3 + l(l+1)/2$. $\tag{21}$

To evaluate $-\xi Y_{1,0}b_{k-1}$, we use the identity

$$Y_{1,0}Y_{m,0} = [(m+1)/(2m+1)]Y_{m+1,0} + [m/(2m+1)]Y_{m-1,0} \tag{22}$$

to obtain after some manipulation of dummy indices

$$-\sum_l Y_{l,0}\left(\frac{l}{2l-1}\sum_{j1}^{2k-1}B(k-1,l-1,j-1)\xi^j + \Theta[(k-2)-l]\frac{l+1}{2l+3}\sum_{l+2}^{2k-1}B(k-1,l+1,j-1)\xi^j\right), \tag{23}$$

where $j1 = l$ for $l \neq 1$, $j1 = 3$ for $l = 1$ and we define

$$\Theta(x) = 1 \text{ for } x \geq 0, \quad \Theta(x) = 0 \text{ for } x < 0. \tag{24}$$

The Θ function is a way of reminding us that the term $l = k$ does not enter the second sum. In a similar manner, the energy term in Eq. (19)

$$\sum_{m=1}^{(k/2)\text{int}} E_{2m} \sum_{l}^{k-2m} Y_{l,0} \sum_{j_l}^{2(k-2m)} B(k-2m,l,j)\xi^j \tag{25}$$

with l odd or even as k is odd or even, can be expressed as

$$\sum_{l}^{k}\left[Y_{l,0}\Theta[(k-2)-l]\sum_{j_l}^{2(k-2)}\left(\sum_{m=1}^{[\frac{1}{2}(k-1)]\text{int}}\Theta[(k-2m)-l]\,\Theta[(2k-4m)-j]\,E_{2m}B(k-2m,l,j)\right)\xi^j\right]+E_k Y_{0,0}. \tag{26}$$

Note that all the terms of Eq. (19) [Eq. (20), Eq. (23), Eq. (26)] now have $\sum_{l}^{k} Y_{l,0}$ with l taking on the values $k, k-2, \ldots, 0(1)$ for k even (odd). Thus for each value of l, we demand that the coefficient of $Y_{l,0}$ vanish. Writing the final form of Eq. (19), setting each coefficient of $Y_{l,0}$ equal to 0, the $B(k,l,j+1)$ for particular values of k and l can be obtained recursively by setting the coefficients of ξ^j in the equation

$$\left(\sum_{j_l-1}^{2k-1} (j+1)B(k,l,j+1) + \sum_{j_l-2}^{2k-2} A(l,j)B(k,l,j+2) - \frac{l}{2l-1}\sum_{j1}^{2k-1} B(k-1,l-1,j-1)\right.$$

$$-\Theta[(k-2)-l]\frac{l+1}{2l+3}\sum_{l+2}^{2k-1} B(k-1,l+1,j-1)+\Theta[(k-2)-l]\sum_{j_l}^{2(k-2)}\sum_{m=1}^{[\frac{1}{2}(k-1)]\text{int}}\Theta[(k-2m)-l]$$

$$\times \Theta[(2k-4m)-j]\,E_{2m}B(k-2m,l,j)+E_k\delta_{l,0}\delta_{j,0}\Big)\xi^j = 0 \tag{27}$$

successively equal to zero starting with $j=2k-1$ and decreasing finally to $j=j_l-1$. The lower limit of j_l-2 in the second sum does not enter since it is readily observed that

$$A(l,l-2)=0, \tag{28}$$

except in the $l=0$ case when the lower limit gives a contribution to the ξ^0 term. Since $A(0,0)=-3$, setting the coefficient of the $l=0$, $j=0$ term equal to zero gives the result

$$E_k = 3B(k,0,2). \tag{29}$$

The $B(k,l,j)$ and E_k have been calculated in double precision through tenth order on the IBM 360MOD50 computer. The expression for the energy is given in the next section and a table of $B(k,l,j)$ is given (Table I) through sixth order.

IV. THE IONIZATION FIELD

The expression for the energy through tenth order is found to be

$$E = -Z^2[.5 + (2.25)\epsilon^2 + (55.546\,875)\epsilon^4$$

$$+ (4.907\,771\,484\times10^3)\epsilon^6 + (7.942\,369\,264\times10^5)\epsilon^8$$

$$+ (1.945\,319\,604\times10^8)\epsilon^{10}]. \tag{30}$$

Thus the ground-state energy in the presence of an electric field is lowered as a result of the induced multipole moments interacting with the electric field. Looking along the field direction (x), the potential energy becomes

$$V(x) = -\lambda x - Z/|x| \tag{31}$$

and at the point

$$x = (Z/\lambda)^{1/2}, \tag{32}$$

$V(x)$ for positive x has its maximum value

$$V_{\text{max}} = -2\lambda^{1/2}Z^{1/2}. \tag{33}$$

This maximum decreases with increasing electric field at a faster rate than the energy E [Eq. (30)], so that when λ is such that E equals V_{max} the system will be ionized. This occurs when

$$\lambda = (1/4Z)E^2 \tag{34}$$

and gives an upper bound to the ionization field since the effect of tunneling which will occur at lower fields has been neglected. Using Eq. (34) we obtain an ionization field in the case of hydrogen of 0.065 35 a.u. For such a large value of the electric field, the tenth-order term in Eq. (30) is found to give a slightly larger correction than the eighth-order term. Therefore the asymptotic series in this case is truncated after eight terms. Our result compares favorably with a recent two parameter variational calculation result[11] of 0.065 a.u. and a field emission experiment[12] which indicates that at a field strength of about 3×10^8 V/cm (0.0585 a.u.) the ion H^+ predominated. Our result is significantly smaller than the WKB result of Rice and Good,[13] who quote a value of the ionization field of about 0.14 a.u. – above this value they found the ground-state wave function is everywhere oscillatory.

LAWRENCE B. MENDELSOHN

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TABLE I. Perturbation wave function coefficients $B(k,l,j)$. Although the calculations were done to tenth order, for brevity the results are reproduced only to sixth order. The large number of significant figures kept are of importance for doing tenth-order expectation value calculations.

k	l	j	$B(k,l,j)$
1	1	1	$0.100\,000\,000\,0 \times 10^{+1}$
1	1	2	$0.500\,000\,000\,0$
2	0	2	$0.750\,000\,000\,0$
2	0	3	$0.250\,000\,000\,0$
2	0	4	$0.416\,666\,666\,7 \times 10^{-1}$
2	2	2	$0.625\,000\,000\,0$
2	2	3	$0.416\,666\,666\,7$
2	2	4	$0.833\,333\,333\,3 \times 10^{-1}$
3	1	1	$0.662\,500\,000\,0 \times 10^{+1}$
3	1	2	$0.331\,250\,000\,0 \times 10^{+1}$
3	1	3	$0.177\,500\,000\,0 \times 10^{+1}$
3	1	4	$0.716\,666\,666\,7$
3	1	5	$0.133\,333\,333\,3$
3	1	6	$0.125\,000\,000\,0 \times 10^{-1}$
3	3	3	$0.350\,000\,000\,0$
3	3	4	$0.262\,500\,000\,0$
3	3	5	$0.750\,000\,000\,0 \times 10^{-1}$
3	3	6	$0.833\,333\,333\,3 \times 10^{-2}$
4	0	2	$0.185\,156\,250\,0 \times 10^{+2}$
4	0	3	$0.617\,187\,500\,0 \times 10^{+1}$
4	0	4	$0.179\,947\,916\,7 \times 10^{+1}$
4	0	5	$0.443\,750\,000\,0$
4	0	6	$0.819\,444\,444\,4 \times 10^{-1}$
4	0	7	$0.902\,777\,777\,8 \times 10^{-2}$
4	0	8	$0.520\,833\,333\,3 \times 10^{-3}$
4	2	2	$0.125\,703\,125\,0 \times 10^{+2}$
4	2	3	$0.838\,020\,833\,3 \times 10^{+1}$
4	2	4	$0.316\,145\,833\,3 \times 10^{+1}$
4	2	5	$0.947\,916\,666\,7$
4	2	6	$0.199\,652\,777\,8$
4	2	7	$0.243\,055\,555\,6 \times 10^{-1}$
4	2	8	$0.148\,809\,523\,8 \times 10^{-2}$
4	4	4	$0.187\,500\,000\,0$
4	4	5	$0.150\,000\,000\,0$
4	4	6	$0.500\,000\,000\,0 \times 10^{-1}$
4	4	7	$0.833\,333\,333\,3 \times 10^{-2}$
4	4	8	$0.595\,238\,095\,2 \times 10^{-3}$
5	1	1	$0.398\,367\,187\,5 \times 10^{+3}$
5	1	2	$0.199\,183\,593\,8 \times 10^{+3}$
5	1	3	$0.937\,640\,625\,0 \times 10^{+2}$
5	1	4	$0.351\,687\,500\,0 \times 10^{+2}$
5	1	5	$0.865\,178\,571\,4 \times 10^{+1}$
5	1	6	$0.176\,737\,351\,2 \times 10^{+1}$

TABLE I (continued)

k	l	j	$B(k,l,j)$
5	1	7	$0.290\,376\,984\,1$
5	1	8	$0.353\,670\,634\,9 \times 10^{-1}$
5	1	9	$0.275\,297\,619\,0 \times 10^{-2}$
5	1	10	$0.111\,607\,142\,9 \times 10^{-3}$
5	3	3	$0.148\,843\,750\,0 \times 10^{+2}$
5	3	4	$0.111\,632\,812\,5 \times 10^{+2}$
5	3	5	$0.421\,093\,750\,0 \times 10^{+1}$
5	3	6	$0.110\,781\,250\,0 \times 10^{+1}$
5	3	7	$0.219\,791\,666\,7$
5	3	8	$0.307\,291\,666\,7 \times 10^{-1}$
5	3	9	$0.266\,203\,703\,7 \times 10^{-2}$
5	3	10	$0.115\,740\,740\,7 \times 10^{-3}$
5	5	5	$0.982\,142\,857\,1 \times 10^{-1}$
5	5	6	$0.818\,452\,381\,0 \times 10^{-1}$
5	5	7	$0.297\,619\,047\,6 \times 10^{-1}$
5	5	8	$0.595\,238\,095\,2 \times 10^{-2}$
5	5	9	$0.661\,375\,661\,4 \times 10^{-3}$
5	5	10	$0.330\,687\,830\,7 \times 10^{-4}$
6	0	2	$0.163\,592\,382\,8 \times 10^{+4}$
6	0	3	$0.545\,307\,942\,7 \times 10^{+3}$
6	0	4	$0.158\,645\,507\,8 \times 10^{+3}$
6	0	5	$0.397\,307\,291\,7 \times 10^{+2}$
6	0	6	$0.827\,439\,236\,1 \times 10^{+1}$
6	0	7	$0.139\,006\,696\,4 \times 10^{+1}$
6	0	8	$0.195\,303\,199\,4$
6	0	9	$0.220\,803\,020\,3 \times 10^{-1}$
6	0	10	$0.187\,458\,664\,0 \times 10^{-2}$
6	0	11	$0.105\,406\,746\,0 \times 10^{-3}$
6	0	12	$0.310\,019\,841\,3 \times 10^{-5}$
6	2	2	$0.102\,811\,816\,4 \times 10^{+4}$
6	2	3	$0.685\,412\,109\,4 \times 10^{+3}$
6	2	4	$0.264\,808\,314\,7 \times 10^{+3}$
6	2	5	$0.807\,036\,830\,4 \times 10^{+2}$
6	2	6	$0.192\,429\,005\,5 \times 10^{+2}$
6	2	7	$0.357\,440\,476\,2 \times 10^{+1}$
6	2	8	$0.542\,348\,710\,3$
6	2	9	$0.652\,488\,425\,9 \times 10^{-1}$
6	2	10	$0.582\,320\,601\,9 \times 10^{-2}$
6	2	11	$0.341\,021\,825\,4 \times 10^{-3}$
6	2	12	$0.103\,339\,947\,1 \times 10^{-4}$
6	4	4	$0.142\,307\,477\,7 \times 10^{+2}$
6	4	5	$0.113\,845\,982\,1 \times 10^{+2}$
6	4	6	$0.443\,995\,535\,7 \times 10^{+1}$
6	4	7	$0.114\,434\,523\,8 \times 10^{+1}$
6	4	8	$0.218\,154\,761\,9$
6	4	9	$0.312\,500\,000\,0 \times 10^{-1}$
6	4	10	$0.318\,813\,131\,3 \times 10^{-2}$
6	4	11	$0.207\,431\,457\,4 \times 10^{-3}$
6	4	12	$0.676\,406\,926\,4 \times 10^{-5}$
6	6	6	$0.507\,812\,500\,0 \times 10^{-1}$
6	6	7	$0.435\,267\,857\,1 \times 10^{-1}$
6	6	8	$0.167\,410\,714\,3 \times 10^{-1}$
6	6	9	$0.372\,023\,809\,5 \times 10^{-2}$
6	6	10	$0.507\,305\,194\,8 \times 10^{-3}$
6	6	11	$0.405\,844\,155\,8 \times 10^{-4}$
6	6	12	$0.150\,312\,650\,3 \times 10^{-5}$

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Angular Distribution of Molecular Photoelectrons*

John C. Tully,[†] R. Stephen Berry, and Bryan J. Dalton[‡]

Department of Chemistry and The James Franck Institute, University of Chicago, Chicago, Illinois 60637

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The nonrelativistic differential cross sections for photo-ionization of molecules are derived and are worked out in detail for systems with random orientation. The more important contributions due to electric dipole, electric quadrupole, magnetic dipole, and two-photon (nonresonant) absorption have been included. Processes such as vibrationally induced auto-ionization have been discussed. The significance of these results with regard to the design and interpretation of photo-ionization experiments is also considered. The angular distribution of photoelectrons from H_2 is calculated as an example.

I. INTRODUCTION

The angular distribution of photoelectrons emitted by a randomly oriented set of molecules is, in general, correlated with the polarization and propagation directions of the incident light. Recent measurements of angular distributions of molecular photoelectrons[1] have demonstrated the usefulness of such measurements in obtaining information about initial states of some systems.

It has been well established that *atomic* photoionization, in the electric dipole approximation, yields an angular distribution of the form $\tilde{\alpha} + \tilde{\beta} \times \cos^2\theta$, where θ is measured from the polarization direction of incident linearly polarized light.[2] Reference 2 also states that "Averaging over the rotational orientations of molecules also gives this form." In this paper we derive expressions for the nonrelativistic differential cross sections for photo-ionization of randomly oriented diatomic molecules, giving explicit equations for the coefficients $\tilde{\alpha}$ and $\tilde{\beta}$ in terms of the transition matrix elements. The more important contributions due to electric dipole, electric quadrupole, magnetic dipole and two-photon (nonresonant) absorption have been included. The pure electric dipole contribution is the largest for normal photon intensi-ties. Interference contributions from the next-higher multipoles may affect the differential photo-ionization cross section by a few percent. Processes such as vibrationally induced auto-ionization have also been considered. The resulting expressions indicate the types of information one might be able to obtain from photoelectron angular-distribution measurements and may be helpful in the design of future experiments.

In nuclear physics, problems involving the correlation between directions and polarizations of various radiations are quite common. As a result, the development of formalisms for treating these processes has been very extensive.[3] Although certain nuclei share with molecules the feature of being nonspherical, the method of handling angular distributions from aspheric targets differs in the two cases. In the case of a molecule, the period of rotation is generally long compared with the time scale of the various photoelectronic processes. Consequently we can treat photoejection from a single molecule as if it occurred with the molecule oriented in a fixed direction in space. We may then average the angular distribution over molecular orientations in the sample. In the case of nuclei, the radiative lifetimes are long compared with rotation periods so