DIPOLE MATRIX ELEMENTS IN HELIUM IN THE FIRST ORDER SHIELDING APPROXIMATION*

by

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ABSTRACT

In this paper the first order shielding approximation is used to calculate off-diagonal matrix elements of the dipole moment operator for helium. The transitions considered are the 2'S--2'P and the 1'S--2'P transitions. When compared with Pekeris' accurate theoretical values, the results calculated here are in error by about 5 per cent for the 2'S--2'P transition and by about 15 per cent for the 1'S--2'P transition.

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I. Introduction

In this paper the first order shielding approximation[1] is used to calculate off-diagonal matrix elements of the dipole moment operator for helium.[2] It has been shown that by using an interchange theorem, the values of off-diagonal matrix elements of one-particle operators can be calculated exactly through first order in the perturbation.[3]

Let W be the operator, and let the Hamiltonian be the sum of an unperturbed Hamiltonian and a perturbation,

$$H = H_0 + \lambda V \quad . \tag{1}$$

Then if M is used to denote the matrix element of the operator, W, between the state p, denoted by Ψ_p, and the state q, denoted by Ψ_q,

$$M = \langle \Psi_p, W \Psi_q \rangle \quad , \tag{2}$$

the value of M through first order in λ, as given by the interchange theorem is

$$M = M^{(0)} + \lambda \left[\langle \Psi_p^{(0,0)}, (V - \epsilon_p^{(1,0)}) \Psi_p^{(0,1)} \rangle + \langle \Psi_q^{(0,1)}, (V - \epsilon_q^{(1,0)}) \Psi_q^{(0,0)} \rangle \right] \quad . \tag{3}$$

The functions $\Psi_p^{(0,0)}$ and $\Psi_q^{(0,0)}$ are eigenfunctions of the unperturbed Hamiltonian, H_0,

$$M^{(0)} = \langle \psi_p^{(0,0)}, W \psi_q^{(0,0)} \rangle \quad , \tag{4}$$

$$\epsilon_p^{(1,0)} = \langle \psi_p^{(0,0)}, V \psi_p^{(0,0)} \rangle \quad , \tag{5}$$

$$\epsilon_q^{(1,0)} = \langle \psi_q^{(0,0)}, V \psi_q^{(0,0)} \rangle \quad , \tag{6}$$

and the wave functions are chosen to be real so that M is also real. The functions $\psi_p^{(0,1)}$ and $\psi_q^{(0,1)}$ are solutions of first order perturbation differential equations,

$$(H_o - \epsilon_p^{(0,0)}) \psi_p^{(0,1)} = -W \psi_q^{(0,0)} + M^{(0)} \psi_p^{(0,0)} \tag{7}$$

and

$$(H_o - \epsilon_q^{(0,0)}) \psi_q^{(0,1)} = -W \psi_p^{(0,0)} + M^{(0)} \psi_q^{(0,0)} \quad , \tag{8}$$

where $\epsilon_p^{(0,0)}$ and $\epsilon_q^{(0,0)}$ are eigenvalues of H_o corresponding to the p and q states respectively. If the differential equations, Eqs. (7) and (8), are solved, the integrals in Eq. (3) can then be performed to determine M.

II. Methods of Solving the Differential Equations.

The differential equations involved in this work can all be expressed in the form

$$\left(-\frac{1}{2}\nabla^2 - \frac{\zeta}{r} - \epsilon\right) U(r,\theta) = h(r,\theta)\, e^{-\alpha r} \quad . \tag{9}$$

The solution and inhomogeneity can be expanded in terms of Legendre polynomials,

$$U(r,\theta) = \sum_{\ell=0}^{\infty} u_\ell(r)\, P_\ell(\cos\theta) \tag{10}$$

and

$$h(r,\theta) = \sum_{\ell=0}^{\infty} h_\ell(r)\, P_\ell(\cos\theta) \quad , \tag{11}$$

which results in an ordinary differential equation for each amplitude, u_ℓ , in Eq. (10). To satisfy boundary conditions the solutions of the homogeneous differential equations, those for which h_ℓ is zero, must be either the radial parts of simple hydrogenic functions or zero. The inhomogeneous differential equations involved can all be expressed in the form,

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{\zeta}{r} + \frac{\ell(\ell+1)}{2r^2} - \epsilon\right] u_\ell(r) = h_\ell(r)\, e^{-\alpha r} \quad . \tag{12}$$

For the purpose of making a power series solution more easily obtainable the left hand side of this equation is transformed to the standard Kummer form of the confluent hypergeometric differential equation. This results in a two-term recursion relation for the coefficients in the power series solution, whereas if the differential equation had been treated in the form of Eq. (12), a power series solution would involve a three-term recursion relation for the coefficients. In addition, the homogeneous solutions of the transformed equation, the Kummer functions, are available in the literature even if ϵ is not a hydrogenic eigenvalue.[4] In order to carry out this transformation, the independent and dependent variables are transformed as follows:

$$r = \frac{1}{2\sqrt{-2\epsilon}}\,\chi \tag{13}$$

$$u_\ell = \chi^\ell\, e^{-\frac{\chi}{2}}\, y(\chi) \tag{14}$$

Then Eq. 12 is transformed to the differential equation

$$\chi y'' + (2\ell+2-\chi)y' - (\ell+1-\frac{\zeta}{\sqrt{-2\epsilon}})\,y$$
$$= \frac{1}{4\epsilon}\,\chi^{-(\ell-1)}\, e^{-\frac{1}{2}(-1+\frac{\alpha}{\sqrt{-2\epsilon}})\chi}\, h_\ell\left(\frac{\chi}{2\sqrt{-2\epsilon}}\right), \tag{15}$$

the homogeneous part of which is in the Kummer form.

The general solution of this differential equation will contain two arbitrary coefficients, each of which multiplies one solution of the homogeneous equation. In any specific case which follows, at least one of these coefficients is determined by boundary conditions placed upon the solution of Eq. (9). The other may remain arbitrary, in which case its value has no effect on the value of the matrix element, M.

III. The 2'S - 2'P Transition.

To calculate the off-diagonal matrix element of the total dipole moment operator for this transition, between a ^1S state and a ^1P state, it is only necessary to know the off-diagonal matrix element of the z-component of the dipole moment operator between the states in question. The matrix element will be calculated to first order using the perturbation method described in the introduction. For this purpose the following definitions are made:[5]

$$W = z_1 + z_2 = r_1 \cos\theta_1 + r_2 \cos\theta_2 \quad ; \tag{16}$$

$$H_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{\zeta}{r_1} - \frac{\zeta}{r_2} \quad ; \tag{17}$$

$$\lambda V = \frac{1}{r_{12}} + \frac{\zeta - 2}{r_1} + \frac{\zeta - 2}{r_2} \quad ; \tag{18}$$

$$\psi_p^{(0,0)} = \frac{1}{\sqrt{2}} \left(1s(1)2s(2) + 2s\,1s(2) \right) \quad ; \tag{19}$$

$$\psi_q^{(0,0)} = \frac{1}{\sqrt{2}} \left(1s(1)2p_z(2) + 2p_z(1)\,1s(2) \right) \; ; \tag{20}$$

$$\epsilon_p^{(0,0)} = \epsilon(1s) + \epsilon(2s) = -\frac{5}{8}\zeta^2 \quad ; \tag{21}$$

$$\epsilon_q^{(0,0)} = \epsilon(1s) + \epsilon(2p) = -\frac{5}{8}\zeta^2 \quad . \tag{22}$$

Here $\psi_q^{(0,0)}$ belongs to a degenerate set, but since the operator in question is the z-component of the dipole moment operator, the only non-vanishing contribution to the matrix element will come from that function selected in Eq. (20).[6] In addition, $M^{(0)}$, as defined by Eq. (4), can be calculated with the unperturbed wave functions for this transition (Eqs. (19) and (20) and has the value

$$M^{(0)} = -\frac{3}{\zeta} \quad . \tag{23}$$

With these definitions the differential equations which must be solved (Eqs. (7) and (8)) become

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{\zeta}{r_1} - \frac{\zeta}{r_2} - \epsilon(1s) - \epsilon(2s)\right)\psi_p^{(0,1)}$$
$$= -\left(r_1\cos\theta_1 + r_2\cos\theta_2\right)\frac{1}{\sqrt{2}}\left(1s(1)2p_z(2) + 2p_z(1)\,1s(2)\right)$$
$$-\frac{3}{\zeta}\frac{1}{\sqrt{2}}\left(1s(1)2s(2) + 2s(1)\,1s(2)\right) \quad , \tag{24}$$

and

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{\zeta}{r_1} - \frac{\zeta}{r_2} - \epsilon(1s) - \epsilon(2p)\right)\psi_q^{(0,1)}$$
$$= -\left(r_1\cos\theta_1 + r_2\cos\theta_2\right)\frac{1}{\sqrt{2}}\left(1s(1)2s(2) + 2s(1)\,1s(2)\right)$$
$$-\frac{3}{\zeta}\frac{1}{\sqrt{2}}\left(1s(1)2p_z(2) + 2p_z(1)\,1s(2)\right) \quad . \tag{25}$$

Each of these equations can be partially separated. The solution of Eq. (24) can be written

$$\psi_p^{(0,1)} = \frac{1}{\sqrt{2}}\left(a(1)2p_z(2) + b(1)1s(2) + 2p_z(1)a(2) + 1s(1)\,b(2)\right) \quad , \tag{26}$$

where a(1) is a solution of the differential equation,

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{\zeta}{r_1} - \epsilon(1s)\right)a(1) = -r_1\cos\theta_1\,1s(1) \quad , \tag{27}$$

and b(1) is a solution of the differential equation,

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{\zeta}{r_1} - \epsilon(2s)\right)b(1) = -r_1\cos\theta_1\,2p_z(1) - \frac{3}{\zeta}2s(1) \quad . \tag{28}$$

The differential equations are solved by the method outlined in section II to give the following solutions:

$$a(1) = \alpha\,1s(1) - \frac{1}{2(\zeta\pi)^{\frac{1}{2}}}\,r_1 e^{-\zeta r_1}\left(2 + \zeta r_1\right)\cos\theta_1 \quad ; \tag{29}$$

and

$$b(1) = \beta 2s(1) + \frac{\zeta^{\frac{1}{2}}}{2\sqrt{2\pi}} \left(r_1^2 - \frac{\zeta r_1^3}{6} \right) e^{-\frac{\zeta r_1}{2}} + \gamma 2p_z(1) + b_2(r_1) P_2(\cos\theta) \quad , \tag{30}$$

where α , β , and γ are arbitrary constants.

The solution of Eq. (25) can be written

$$\psi_g^{(0,1)} = \frac{1}{\sqrt{2}} \left(a(1)2s(2) + c(1)\,1s(2) + 2s(1)a(2) + 1s(1)c(2) \right) \quad , \tag{31}$$

where a(1) is given by Eq. (29), and c(1) is a solution of the differential equation

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{\zeta}{r_1} - \epsilon(2p) \right) c(1) = -r_1 \cos\theta_1 \, 2s(1) - \frac{3}{\zeta} 2p_z(1) \quad , \tag{32}$$

which is

$$c(1) = \eta 2s(1) + \xi 2p_z(1) + \frac{\zeta^{\frac{3}{2}}}{4\sqrt{2\pi}} r_1^3 e^{-\frac{\zeta r_1}{2}} \cos\theta_1 \quad , \tag{33}$$

where η and ξ are arbitrary constants.

The value of M, as given by Eq. (3) can now be calculated with the functions, $\psi_p^{(0,1)}$ and $\psi_g^{(0,1)}$, just determined, the value of $M^{(0)}$ given by Eq. (23), and with λV given by Eq. (18). In carrying out the integration it is seen that $b_2(r_1)$ in Eq. (30) does not affect the value of M, and that the values assigned to the arbitrary constants in all of the functions also are immaterial. The result of the integration is an expression for M as a function

of ζ , the scale factor,

$$M = -\frac{3}{\zeta} + \frac{1}{\zeta^2}\left[-\frac{19,997}{3^8} + (\zeta-2)(-3)\right] \quad . \quad (34)$$

If ζ is set equal to the nuclear charge, 2, the value of M is

$$M(2) = -2.26196464 \quad . \quad (35)$$

A better value for M is obtained by using the shielding approximation, that is, by setting ζ equal to that value which makes all first-order corrections equal to zero. That value of ζ is

$$\zeta = 0.98404715 \quad , \quad (36)$$

and the corresponding value of $M(\zeta) = -\frac{3}{\zeta}$ is

$$M = -3.0486344 \quad . \quad (37)$$

These results can be compared with a value obtained from Pekeris' accurate calculations of the oscillator strength[7] and the energies of the states,[8]

$$|M| = 2.915956 \quad . \quad (38)$$

The value without scaling calculated here differs from this by about 22 per cent and the value with scaling differs by about 4.6 per cent.

Cohen and Dalgarno[2] have discussed the 2^1S--2^1P transition with the Hartree-Fock function. Using the shielding approximation they obtained the value,

$$M = -3.326 \quad . \tag{39}$$

IV. The 1^1S--2^1P Transition

For this transition, as in the case of the 2^1S--2^1P transition, the off-diagonal matrix element of the z-component of the dipole moment operator will be calculated. For this purpose all quantities involved are defined the same as they were in Sect. III (Eqs. (16) through (22)) with the following exceptions:

$$\psi_p^{(0,0)} = 1s(1)\,1s(2) \quad ; \tag{40}$$

$$\epsilon_p^{(0,0)} = 2\epsilon(1s) = -\zeta^2 \quad . \tag{41}$$

In this case, the zeroth-order matrix element, $M^{(0)}$, as defined by Eq. (4), has the value

$$M^{(0)} = \frac{2^8}{3^5\zeta} \quad . \tag{42}$$

Consequently, the differential equations which must be solved (Eqs. (7) and (8)) are

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{\zeta}{r_1} - \frac{\zeta}{r_2} - 2\epsilon(1s)\right)\psi_p^{(0,1)}$$
$$= -(r_1\cos\theta_1 + r_2\cos\theta_2)\frac{1}{\sqrt{2}}\left(1s(1)2p_z(2) + 2p_z(1)1s(2)\right)$$
$$+ \frac{2^8}{3^5\zeta}\,1s(1)1s(2) \quad , \tag{43}$$

and

$$\left(-\frac{1}{2}\nabla_1^2-\frac{1}{2}\nabla_2^2-\frac{\zeta}{r_1}-\frac{\zeta}{r_2}-\epsilon(1s)-\epsilon(2p)\right)\psi_g^{(0,1)}$$

$$=-(r_1\cos\theta_1+r_2\cos\theta_2)\,1s(1)\,1s(2)$$

$$+\frac{2^8}{3^5\zeta}\frac{1}{\sqrt{2}}\left(1s(1)2p_z(2)+2p_z(1)\,1s(2)\right) \quad . \quad (44)$$

Eq. (43) can be partially separated by writing the solution in the form

$$\psi_p^{(0,1)}=\frac{1}{\sqrt{2}}\left(g(1)\,2p_z(2)+t(1)\,1s(2)\right.$$

$$\left.+2p_z(1)\,g(2)+1s(1)\,t(2)\right) \quad , \quad (45)$$

where g(1) is a solution of the differential equation,

$$\left(-\frac{1}{2}\nabla_1^2-\frac{\zeta}{r_1}+\frac{7}{8}\zeta^2\right)g(1)=-r_1\cos\theta_1\,1s(1) \quad , \quad (46)$$

and t(1) is a solution of the differential equation,

$$\left(-\frac{1}{2}\nabla_1^2-\frac{\zeta}{r_1}-\epsilon(1s)\right)t(1)=-r_1\cos\theta_1\,2p_z(1)+\frac{2^7\sqrt{2}}{3^5\zeta}\,1s(1). \quad (47)$$

The solution of Eq. (46) is

$$g(1)=\frac{2}{7\sqrt{5\pi}}\,r_1\,e^{-\frac{\sqrt{7}\zeta r_1}{2}}\sum_{i=0}^{\infty}a_i\left(\sqrt{7}\zeta r_1\right)^i\cos\theta_1 \quad , \quad (48)$$

where a_o = -2.14875649194, and the other coefficients in the power series are given by a simple recursion relation.[9] The solution of Eq. (47) is

$$t(1) = \frac{1}{3\cdot 2^5\sqrt{2\pi}\,\zeta^{\frac{3}{2}}}\, e^{-\zeta r_1} \sum_{i=0}^{\infty} b_i\,(2\zeta r_1)^i + t_2(r_1)\,P_2(\cos\theta_1), \quad (49)$$

where $t_2(r_1)$ contributes nothing to the value of the matrix element, b_0 is arbitrary, and the other coefficients in the power series are given by a two-term recursion relation.

Eq. (44) can be partially separated by writing the solution in the form

$$\psi_g^{(0,1)} = \frac{1}{\sqrt{2}}\left(w(1)\,1s(2) + 1s(1)\,w(2)\right) \quad , \quad (50)$$

where $w(1)$ is a solution of the differential equation,

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{\zeta}{r_1} - \epsilon(2p)\right)w(1) = -\sqrt{2}\,r_1\cos\theta_1\,1s(1) + \frac{2^8}{3^5\zeta}\,2p_z(1) \quad . \quad (51)$$

It follows that

$$w(1) = \alpha\,2s(1) + \frac{2\sqrt{2}}{\sqrt{\zeta\pi}}\,r_1\,e^{-\frac{\zeta r_1}{2}} \sum_{i=0}^{\infty} c_i\,(\zeta r_1)^i\cos\theta_1 \quad , \quad (52)$$

where α is an arbitrary constant, c_0 is arbitrary, and the other coefficients in the power series are given by a recursion relation.

The value of M, as given by Eq. (3), can now be calculated with the functions, $\psi_p^{(0,1)}$ and $\psi_g^{(0,1)}$, just determined, the value of $M^{(0)}$ given by Eq. (42), with λV given by Eq. (18), with $\epsilon_p^{(1,0)}$ and $\epsilon_g^{(1,0)}$ given by Eqs. (5) and (6), and with $\psi_p^{(0,0)}$ and $\psi_g^{(0,0)}$

given by Eqs. (40) and (20). The integrations are carried out by summing over the contributions of the separate terms in the power series solutions. The result of the integration is an expression for M as a function of ζ, the scale factor

$$M = \frac{2^8}{3^5\zeta} - \frac{0.163270218}{\zeta^2} + \frac{2^8}{3^5}\frac{(\zeta-2)}{\zeta^2} \quad . \tag{53}$$

If ζ is set equal to the nuclear charge, 2, the value of M is

$$M(2) = 0.4859314165 \quad . \tag{54}$$

A slightly <u>worse</u> value for M is obtained by setting ζ equal to that value which makes all first-order corrections equal to zero. That value of ζ is

$$\zeta = 2.154979152 \quad , \tag{55}$$

and the corresponding value of $M(\zeta) = \frac{2^8}{3^5\zeta}$ is

$$M = 0.488866883 \quad . \tag{56}$$

These results can be compared with the value obtained from Pekeris' calculations,[10]

$$|M| = 0.420776 \quad . \tag{57}$$

The value without scaling calculated here differs by about 15 per cent and the value with scaling differs by about 16 per cent. Thus if no mistake was made in the integration or other work related to the 1^1S--2^1P transition, one must conclude that scaling does not always bring about an improvement.

FOOTNOTES

1. See A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. A257, 534 (1960).

2. Off-diagonal matrix elements for transitions of the type $1s^a 2s^b 2p^c -- 1s^a 2s^{b-1} 2p^{c+1}$ have been calculated using perturbation methods within the Hartree-Fock formalism for all members of iso-electronic sequences from helium to neon. See M. Cohen and A. Dalgarno, Proc. Roy. Soc. A280, 258 (1964).

3. See M. Cohen and A. Dalgarno, Proc. Roy. Soc. A275, 492 (1963); S. Borowitz and M. Vassell, JQSRT 4, 663 (1964); Joseph O. Hirschfelder, W. Byers Brown, and Saul T. Epstein, "Recent Developments in Perturbation Theory", Advances in Quantum Chemistry, Vol. 1 (Academic Press, New York, 1964), Chapter VIII, p. 315.

4. See Lucy Joan Slater, Confluent Hypergeometric Functions (Cambridge University Press, Cambridge, 1960); Lucy Joan Slater, "Confluent Hypergeometric Functions", Handbook of Mathematical Functions (National Bureau of Standards, Washington, 1964), Chap. 13, p. 503.

5. Hartree atomic units are used throughout this paper. In this system one unit of energy=1 hartree=27.2097 e.v.

6. For a discussion of degeneracy see Hirschfelder, et. al., op. cit., p. 318, footnote No. 23.

7. See B. Schiff and C. L. Pekeris, Phys. Rev. 134, A638 (1964).

8. For the 2'S energy see C. L. Pekeris, Phys. Rev. 126, 1470 (1962); for the 2'P energy see C. L. Pekeris, B. Schiff, and H. Lifson, Phys. Rev. 126, 1057 (1962).

9. The value of a_o and the values of the integrals which follow were calculated by numerically summing the terms in the exact infinite series expressions using a Control Data Corporation G15 computer.

10. See Footnotes No. 7 and No. 8 above; also for the 1'S energy see C. L. Pekeris, Phys. Rev. 115, 1216 (1959).