PHYSICAL REVIEW B **70**, 085210 (2004)

Stark shifts of 2*p* hydrogenic states in magnetic fields

David M. Larsen
University of Massachusetts Lowell, Lowell, Massachusetts 01854, USA

(Received 8 September 2003; published 26 August 2004)

Energy shifts in a magnetic field of hydrogenic $2p_{-1}$ and $2p_0$ levels induced by weak external applied electric fields are calculated by approximate evaluation of the appropriate second-order perturbation theory expressions. Results are tabulated over a range of magnetic fields of experimental interest and combined with a calculation of the shifts of the 1*s* level energy to give Stark shifts of the $1s\rightarrow 2p_{-1}$ and the $1s\rightarrow 2p_0$ transitions. These latter quantities are of importance in interpreting line shape data in the magnetospectroscopy of shallow donors in partially compensated GaAs and related semiconductors.

DOI: 10.1103/PhysRevB.70.085210 PACS number(s): 78.30.Fs, 32.60.+i

I. INTRODUCTION

Magneto-optical experiments on shallow donors in high-purity partially compensated n-type GaAs at low temperatures reveal sharp strong lines arising from transitions from the 1*s* ground state to the 2*p* levels. The wave functions for these levels are very well described by effective mass theory. The transitions, especially the $1s\rightarrow 2p_{-1}$ transition, show asymmetric broadenings with tails appearing on the low-energy side characteristic of Stark-effect broadening.[1,2] Electric fields responsible for Stark broadening arise from the donor and acceptor ions present in compensated samples. Quantitative understanding of the breadths of these lines can give important information on correlations between neutral and ionized donor sites at low lattice temperatures.

To calculate the portion of this broadening due to the quadratic Stark effect one would like to evaluate energy shifts in the relevant donor levels induced by the more or less random weak electric fields at the locations of the various neutral donors. Over a range of applied magnetic fields of interest this can be done, in principle, by second-order perturbation theory, treating the electric field as a perturbation and using the eigenstates of hydrogenic atoms in a magnetic field as the unperturbed wave functions. Unfortunately an exact evaluation of the perturbation expressions by direct calculation seems prohibitively difficult. In this paper an approximate evaluation of the second-order perturbation series for the $2p_0$ and $2p_{-1}$ levels is attempted by a well-known variational method, which has been applied earlier to the 1*s* level.[3] A calculation of this type has already been carried out[4] for the $2p_{-1}$ level, but the slow convergence of the method employed and the relatively inaccurate $2p_{-1}$ wave functions utilized impair the accuracy of that calculation. Moreover, the results are presented only graphically and in such a way to make it difficult to extract quantitative values. No previously published results for the $2p_0$ level appear to be available.

Above and henceforth each state of the hydrogen atom in a magnetic field is designated by the name of the state at zero magnetic field from which it evolves when the magnetic field is turned on adiabatically; abbreviations used are $2p_-$ for $2p_{-1}$ and $2p_+$ for $2p_{+1}$ states. The present paper presents tabulated polarizabilities of the hydrogenic $2p_-$ and $2p_0$ levels. Typical expected accuracies are estimated to be approximately 1%; the calculations are believed to be most accurate at the lower end of the range of magnetic fields considered.

II. PERTURBATION CALCULATIONS

The unperturbed hamiltonian H_0 describing a simple hydrogenic donor in a uniform magnetic field in the *z* direction *B* is given in the units of this paper by

$$H_0 = -\nabla^2 - 2/r + (\gamma/i)\,\partial/\partial\phi + \gamma^2\rho^2/4. \tag{1}$$

The electric field perturbation is

$$\begin{aligned} H' &= \vec{F}\cdot\vec{r} = F_+(x+iy) + F_-(x-iy) + F_z z \\ &= H'^{(+)} + H'^{(-)} + H'^{(z)}, \end{aligned} \tag{2}$$

where

$$H'^{(+)} = 0.5F_+\rho e^{i\phi}, \tag{3a}$$

$$H'^{(-)} = 0.5F_-\rho e^{-i\phi}, \tag{3b}$$

$$H'^{(z)} = F_z z \tag{3c}$$

with $F_+=F_x-iF_y$ and $F_-=F_x+iF_y$. The dimensionless electric force vector $\vec{F}$ is given by $\vec{F}=-e\vec{E}a_0/\mathrm{Ry}$, where $\vec{E}$ is the uniform electric field, a_0 is the donor bohr radius, and Ry is the donor Rydberg ($a_0=\epsilon_0\hbar^2/m^*e^2$, $\mathrm{Ry}=e^2/2\epsilon_0 a_0$, m^* is the conduction band mass and ϵ_0 is the static dielectric constant). The magnetic field has been introduced as usual via the vector potential $\vec{A}=B(-y/2,x/2,0)$. It appears in Eq. (1) in the dimensionless parameter γ, which is defined by $\gamma=\hbar eB/(2m^*cRy)$. In Eq. (1) and henceforth (unless otherwise specified) lengths are taken in units of a_0 and energies in units of Ry.

The normalized eigenstates of H_0 are labeled φ_n, with the unperturbed energies E_n defined by $H_0\varphi_n=E_n\varphi_n$. These eigenstates can be classified according to their angular momentum quantum number *M* along the direction of the magnetic field (*z* direction) and by their *z*-parity quantum number P_z; $P_z=+1$ for eigenstates which do not change sign upon reflection of coordinates through the x-y plane $(z\rightarrow -z)$ whereas $P_z=-1$ for those that do.

The energy shift of a 2*p* state can be written in second-order Rayleigh-Schrodinger perturbation theory as

$$\Delta E_{2p} = \sum_n \frac{|H'_{2p,n}|^2}{E_{2p} - E_n} = \alpha_\perp^{(2p)} F_\perp^2 + \alpha_z^{(2p)} F_z^2 \tag{4}$$

with $F_\perp^2 = F_x^2 + F_y^2$. Calculation of the polarizabilities $\alpha_\perp^{(2p)}$ and $\alpha_z^{(2p)}$ is the principal goal of this paper.

The sum in Eq. (4) is over all possible intermediate states n. For the $2p_-$ state, which has $M=-1$ and $P_z=+1$, the intermediate states appearing in Eq. (4) fall into three categories, the set of states, designated $S_{-1,-1}$, with $M=-1$ and $P_z=-1$ [which are coupled to $2p_-$ via the term $F_z z$ in Eq. (2)], the set $S_{-2,1}$, with $M=-2$ and $P_z=+1$ (coupled by the term $0.5F_- \rho e^{-i\phi}$), and the set $S_{0,1}$, with $M=0$ and $P_z=+1$, (coupled via $0.5F_+ \rho e^{i\phi}$). It is useful to segregate the terms appearing in the summation in Eq. (4) according to the character of the intermediate states. Thus one can write

$$\Delta E_{2p_-} = \Delta E_{2p_-}^{(1)} + \Delta E_{2p_-}^{(2)} + \Delta E_{2p_-}^{(3)}, \tag{5}$$

where

$$\Delta E_{2p_-}^{(1)} = \sum_{S_{-1,-1}} \frac{|H'_{2p_-,n}|^2}{E_{2p_-} - E_n} = \sum \frac{|H'^{(z)}_{2p_-,n}|^2}{E_{2p_-} - E_n} = \alpha_z^{(2p_-)} F_z^2, \tag{6a}$$

$$\Delta E_{2p_-}^{(2)} = \sum_{S_{-2,1}} \frac{|H'_{2p_-,n}|^2}{E_{2p_-} - E_n} = \sum \frac{|H'^{(-)}_{2p_-,n}|^2}{E_{2p_-} - E_n} = \beta(-2,1) F_\perp^2, \tag{6b}$$

$$\Delta E_{2p_-}^{(3)} = \sum_{S_{0,1}} \frac{|H'_{2p_-,n}|^2}{E_{2p_-} - E_n} = \sum \frac{|H'^{(+)}_{2p_-,n}|^2}{E_{2p_-} - E_n} = \beta(0,1) F_\perp^2, \tag{6c}$$

$$\beta(-2,1) + \beta(0,1) = \alpha_\perp^{(2p_-)}. \tag{6d}$$

In Eqs. (6a)–(6c) the notation $\Sigma s_{i,j}$ means summation over all and only intermediate states belonging to set $S_{i,j}$. It is known that, aside from the $1s$ donor ground state, the $2p_-$ state has, for nonzero magnetic field, the lowest energy of any donor level appearing in the perturbation theory expressions above.[5] As a result all energy denominators in Eqs. (6a) and (6b) are negative whereas one energy denominator is positive (for the $1s$ intermediate state) in Eqs. (4) and (6c).

Direct exact evaluation of the perturbation sums in Eqs. (6a)–(6c) is not feasible. One can show, however, that these perturbation sums are derivable from a variational principle. For any perturbation H' [not necessarily the one defined by Eq. (2) above] the stationary value of the energy functional $F(\Psi)$ defined by

$$F(\Psi) = \int \Psi^* (H_0 - E_{2p_{-1}})\Psi + \int (\Psi^* H' \varphi_{2p_{-1}} + \text{c.c.}) \tag{7}$$

is equal to the required second-order perturbation expression. To show this one can expand Ψ in the eigenstates of H_0, obtaining

$$\Psi = \sum_i c_i \varphi_i$$

and

$$F(\Psi) = \sum |c_i|^2 (E_i - E_{2p_-}) + \sum (c_i^* H'_{i,2p_-} + \text{c.c.}). \tag{8}$$

Setting the first derivatives of the right-hand side of Eq. (8) with respect to the real part and to the imaginary part of c_i equal to zero for each value of i, solving the resulting (trivial) linear equations for the coefficients c_i and substituting the results into the right-hand side of Eq. (8) leads to the standard second-order perturbation series. Notice that this procedure finds a minimum of $F(\Psi)$ if and only if

$$H'_{1s,2p_-} = 0 \tag{9}$$

(which is satisfied if H' is taken to be either $H'^{(-)}$ or $H'^{(z)}$), for in that case $c_{1s}=0$. Otherwise $F(\Psi)$ has no lower bound.

As a rule one does not know $\Psi_{\min}$, the function minimizing $F(\Psi)$ (when a minimum exists). One can proceed by approximating $\Psi_{\min}$ by a trial function Ψ which contains variational parameters. For those cases in which Eq. (9) is satisfied a choice of Ψ which differs from the $\Psi_{\min}$ by a small function of order ϵ_Ψ will produce, when substituted into Eq. (7), a value which differs from the exact second-order perturbation correction by an amount only of order ϵ_Ψ^2. This desirable situation occurs for $\Delta E_{2p_-}^{(1)}$ and $\Delta E_{2p_-}^{(2)}$ but not for $\Delta E_{2p_-}^{(3)}$ in Eqs. (6a)–(6c).

In the event that Eq. (9) does not hold one can still retain the sought-for property that first-order errors in Ψ lead to second-order errors in the energy functional simply by orthogonalizing Ψ to φ_{1s}. Thus if the orthogonalized function $\tilde{\Psi}$ is defined by

$$\tilde{\Psi} = \Psi - \langle \varphi_{1s} | \Psi \rangle \varphi_{1s} \tag{10}$$

then one can define the functional $\tilde{F}(\Psi) = F(\tilde{\Psi})$, which has a minimum value $\tilde{F}_{\min}$ such that the second-order energy shift is given by

$$\Delta E_{2p_-} = \tilde{F}_{\min} + \frac{|H'_{1s,2p_-}|^2}{E_{2p_-} - E_{1s}}. \tag{11}$$

In the present paper $\Psi_{\min}$ is approximated by Ψ, which is expanded as a linear combination of certain functions; functionals $F(\Psi)$ are then evaluated and minimized with respect to the expansion coefficients for calculations of $\Delta E_{2p_-}^{(1)}$ and $\Delta E_{2p_-}^{(2)}$ of Eqs. (6a) and (6b). On the other hand $\tilde{F}(\Psi)$ is minimized and Eq. (11) used for evaluating $\Delta E_{2p_-}^{(3)}$ of Eq. (6c). In contrast, the calculations of Ref. 4, which use similar approximations to $\Psi_{\min}$, determine the coefficients of expansion by rendering the functionals $F(\Psi)$ stationary with respect to variations of these coefficients. The two approaches are equivalent for $\Delta E_{2p_-}^{(1)}$ and $\Delta E_{2p_-}^{(2)}$ but not for $\Delta E_{2p_-}^{(3)}$. In this latter case the error of the present paper due to errors in the approximation to Ψ is of second order whereas that of Ref. 4 can be expected to be of first order.

Probably the primary source of error in the present calculation, however, arises from the fact that exact expressions in closed form are lacking for any of the unperturbed wave functions $\varphi_{2p_{-1}}$, φ_{2p_0}, or φ_{1s}; approximations to these functions are required for evaluating $F(\Psi)$ or $\widetilde{F}(\Psi)$. Errors in these unperturbed functions which are of order ϵ_φ produce errors in the calculated second order energy correction of the same order. In the present paper separate variational calculations are carried out for these approximate unperturbed functions, denoted $\varphi^{(A)}$. Although wave functions for only the 2p states listed above and the 1s state are required for the polarizability calculations, wave functions for certain additional states are useful for estimating upper and lower bounds on the polarizabilities, as will be described. The multiparameter unperturbed wave functions employed in this paper are of the form

$$\varphi_{1s}^{(A)} = \xi_{1s}(\rho,z), \tag{12a}$$

$$\varphi_{2p_-}^{(A)} = \rho e^{-i\phi}\xi_{2p_-}(\rho,z), \tag{12b}$$

$$\varphi_{2p_0}^{(A)} = z\xi_{2p_0}(\rho,z), \tag{12c}$$

$$\varphi_{3d_{-1}}^{(A)} = z\rho e^{-i\phi}\xi_{3d_{-1}}(\rho,z), \tag{12d}$$

$$\varphi_{3d_{-2}}^{(A)} = \rho^2 e^{-2i\phi}\xi_{3d-2}(\rho,z), \tag{12e}$$

$$\begin{aligned}\varphi_{2s}^{(A)} = \{&[2 - a_1(\rho^2 + \alpha_1 z^2 + \beta)^{1/2} + a_2\rho^2(\rho^2 + \alpha_2 z^2)^{1/2}]\\ &\times\exp[-H\rho^2/2 - \kappa(\rho^2 + \alpha z^2)^{1/2} - \delta z^2] - D\varphi_{1s}^{(A)}\}/N,\end{aligned} \tag{12f}$$

where

$$\begin{aligned}\xi(\rho,z) = \exp[&-H\rho^2/2 - A(r^2 + Bz^2)^{1/2}\rho^2 - Cz^2\\ &- \kappa(\rho^2 + \alpha z^2 + \beta^2)^{1/2}]/N,\end{aligned}$$

N is the appropriate normalization constant for each state and D is chosen to guarantee that $\varphi_{2s}^{(A)}$ is orthogonal to $\varphi_{1s}^{(A)}$. The parameters are varied separately for each magnetic field strength to minimize the energy of each state in the unperturbed Hamiltonian H_0. The 2p_- state wave function in Eq. (12b) is more general than that employed in Ref. 4, where A and β are set equal to zero and α is set equal to 1. Comparison of the calculated variational unperturbed energies with the extremely accurate energies of Ref. 6 shows that in the range $0.1 < \gamma < 3.0$ the energies obtained from $\varphi_{2p_-}^{(A)}$ of Eq. (12b) differ from the corresponding exact values by amounts which are more than a factor of 10 smaller than those obtained from the wave functions of Ref. 4. At $\gamma = 1$ the variational energy obtained from the wave function given by Eq. (12b) is too high by 0.5×10^{-4} Ry. Errors at smaller fields are smaller and at larger fields, larger. Errors in the 1s energies are typically about half as large as those for 2p_-. Details of the energy errors are presented in Table I. [It seems worth noting that only very small changes in 2s energies were produced by including the term proportional to a_2 in the wave function of Eq. (12f).]

Three trial functions $\Psi^{(i)}$ employed for calculations of the polarizability of the 2p_{-1} state, one for each of the energies $\Delta E_{2p_-}^{(i)}$, defined in Eqs. (6a)–(6c), are displayed in Eqs. (13a)–(13c).

TABLE I. Energy differences between $\langle\varphi^{(A)}|H_0|\varphi^{(A)}\rangle/\langle\varphi^{(A)}|\varphi^{(A)}\rangle$ and the corresponding energies of Ref. 6 in units of 10^{-4} donor Ry. The size of these differences is a measure of the goodness of the approximate wave functions. If the functions $\varphi^{(A)}$ were exact all entries would be zero.

γ	1s	2p_0	2p_{-1}	3d_{-1}	3d_{-2}	2s
0.3	<0.1	<0.1	<0.1	0.25	<0.1	−0.5
0.5	<0.1	0.23	0.29	0.27	0.16	0.6
0.8	<0.1	0.49	0.39	0.41	0.31	0.8
1.0	0.16	0.65	0.52	0.49	0.36	1.0
1.5	0.39	1.0	0.94	0.69	0.60	1.2
2.0	0.71	1.3	1.4	0.81	0.84	1.2
3.0	1.6	1.7	2.3	1.1	1.2	1.0
5.0	3.9	2.1	3.9	1.1	1.6	0.6

$$\begin{aligned}\Psi^{(1)} = F_z[&z(a_0 + a_1 r + a_2 r^2 + a_3 r^3 + a_4 r^4) + z^3(b_0 + b_1 r)\\ &+ z^5 c_0]\varphi_{2p_-}^{(A)},\end{aligned} \tag{13a}$$

$$\begin{aligned}\Psi^{(2)} = F_-[&\rho(a_0 + a_1 r + a_2 r^2) + \rho^3(b_0 + b_1 r + b_2 r^2)\\ &+ \rho^5 c_0]e^{-i\phi}\varphi_{2p_-}^{(A)},\end{aligned} \tag{13b}$$

$$\begin{aligned}\Psi^{(3)} = F_+[&\rho^{-1}(a_0 + a_1 r + a_2 r^2) + \rho(b_0 + b_1 r + b_2 r^2)\\ &+ \rho^3 c_0]e^{i\phi}\varphi_{2p_-}^{(A)}.\end{aligned} \tag{13c}$$

Only $\Psi^{(3)}$ need be explicitly orthogonalized to the 1s ground state wave function since the other two trial functions are orthogonal by symmetry to s states. The procedure for calculating α_z in Eq. (4) for the 2p_{-1} state is to substitute $\Psi^{(1)}$ for Ψ in that equation and minimize the result with respect to the eight variational parameters a, b, and c appearing in Eq. (13a). The minimum value so obtained is divided by F_z^2 to obtain the required estimate of α_z. Since both $\Delta E_{2p_-}^{(2)}$ and $\Delta E_{2p_-}^{(3)}$ contribute to $\alpha_\perp$ it is necessary to perform two separate independent minimizations, one involving $\Psi^{(2)}$ alone and the other involving $\Psi^{(3)}$ othogonalized to $\phi_{1s}^{(A)}$ [see Eq. (10)]. The two minimum values obtained are added together along with the contribution of the 1s state [which is given by the second term on the right-hand side of Eq. (11) with variational wave functions for 1s and 2p_- employed in evaluating the matrix element there]. The result is then divided by $4F_\perp^2$ to obtain $\alpha_\perp$. Values are tabulated in Table II. It should be noted that the terms in Eqs (13a)–(13c) vary very much in the size of their contributions. The largest contributions come from terms involving the smaller powers of z, ρ, and r; some of the higher-power terms prove to be superfluous in many instances.

Very similar calculations have been carried out for the polarizability of the 2p_0 state. The main differences are that the trial functions have the form

$$\begin{aligned}\Psi^{(1)} = F_z[&z^{-1}(a_0 + a_1 r + a_2 r^2 + a_3 r^3 + a_4 r^4) + z(b_0 + b_1 r)\\ &+ z^3 c_0]\varphi_{2p_0}^{(A)},\end{aligned} \tag{14a}$$

TABLE II. Polarizabilities of the hydrogenic $2p_-$ level as defined in Eq. (4) vs dimensionless magnetic field γ. The quantities α_z and $\alpha_\perp$ are for electric fields respectively parallel and perpendicular to the magnetic field.

γ	$\alpha_z^{(2p_-)}$	$\alpha_\perp^{(2p_-)}$	$\beta(0,1)$
0.3	−11.3	−17.9	−3.73
0.5	−7.08	−9.61	−1.06
0.8	−4.48	−5.30	−0.20
1.0	−3.59	−3.97	−0.035
1.5	−2.37	−2.34	0.087
2.0	−1.76	−1.60	0.104
3.0	−1.16	−0.94	0.092
5.0	−0.68	−0.47	0.062

$$\Psi^{(2)} = F_-[\rho(a_0 + a_1 r + a_2 r^2) + \rho^3(b_0 + b_1 r + b_2 r^2) + \rho^5 c_0]e^{-i\phi}\varphi_{2p_0}^{(A)}, \tag{14b}$$

$$\Psi^{(3)} = F_+[\rho(a_0 + a_1 r + a_2 r^2 + a_3 r^3) + \rho^3(b_0 + b_1 r + b_2 r^2) + \rho^5 c_0]e^{i\phi}\varphi_{2p_0}^{(A)}. \tag{14c}$$

Here $\Psi^{(1)}$ is othogonalized to $\phi_{1s}^{(A)}$ and the energy correction due to the $1s$ state is found from Eq. (11) using the variational $2p_0$ wave function. Results are given in Table III.

Finally, for purposes of comparison to the results for the $1s$ state given in Ref. 3, the following trial functions are employed:

$$\Psi^{(1)} = F_z[z(a_0 + a_1 r + a_2 r^2 + a_3 r^3 + a_4 r^4) + z^3(b_0 + b_1 r) + z^5 c_0]\varphi_{1s}^{(A)}, \tag{15a}$$

$$\Psi^{(2)} = F_-[\rho(a_0 + a_1 r + a_2 r^2) + \rho^3(b_0 + b_1 r + b_2 r^2) + \rho^5 c_0]e^{-i\phi}\varphi_{1s}^{(A)}, \tag{15b}$$

TABLE III. Polarizabilities of the hydrogenic $2p_0$ level as defined in Eq. (4) vs dimensionless magnetic field γ. The quantities α_z and $\alpha_\perp$ are for electric fields respectively parallel and perpendicular to the magnetic field.

γ	$\alpha_z^{(2p_0)}$	$\alpha_\perp^{(2p_0)}$
0.3	−104	−12.5
0.5	−66.0	−8.10
0.8	−46.2	−5.30
1.0	−39.5	−4.31
1.5	−30.5	−2.96
2.0	−25.8	−2.27
3.0	−20.8	−1.58
5.0	−16.3	−1.01

TABLE IV. Comparison of polarizabilities of the hydrogenic $1s$ level vs dimensionless magnetic field γ. Quantities $\alpha(P)$ are calculated in the present paper whereas those designated $\alpha(3)$ are taken from Ref. 3.

γ	$\alpha_z(P)$	$\alpha_z(3)$	$\alpha_\perp(P)$	$\alpha_\perp(3)$
0.3	−0.9713	−0.9737	−0.8927	−0.8937
0.5	−0.8384	−0.8366	−0.7099	−0.7110
0.8	−0.6759	−0.6773	−0.5228	−0.5227
1.0	−0.5983	−0.5982	−0.4381	−0.4384
1.5	−0.4618	−0.4629	−0.3051	−0.3050
2.0	−0.377	−0.378	−0.2296	−0.230
3.0	−0.276	−0.277	−0.1494	−0.149
5.0	−0.182	−0.182	−0.0838	−0.083

$$\Psi^{(3)} = F_+[\rho(a_0 + a_1 r + a_2 r^2) + \rho^3(b_0 + b_1 r + b_2 r^2) + \rho^5 c_0]e^{i\phi}\varphi_{1s}^{(A)}. \tag{15c}$$

Obviously no orthogonalization or correction for the $1s$ contribution is required. Results are compared in Table IV to those in Ref. 3. Agreement is closer than 0.25% for all values of γ (except for $\gamma = 5$, where the results in Ref. 3 are quoted to no more than two significant places).

The $1s \to 2p$ transitions in the presence of weak electric fields are shifted from their zero field values by an amount

$$(\alpha_\perp^{(2p)} - \alpha_\perp^{(1s)})F_\perp^2 + (\alpha_z^{(2p)} - \alpha_z^{(1s)})F_z^2. \tag{16}$$

For convenience in interpolating the coefficients of $F_\perp^2$ and F_z^2 in Eq. (16) at values of magnetic field (γ) not appearing in the tables presented here, the tabulated results have been fit by the following interpolation formulas applicable to $1s \to 2p_-$ transitions for $0.3 \leqslant \gamma \leqslant 5.0$:

$$(\alpha_\perp^{(2p_-)} - \alpha_\perp^{(1s)}) = 0.01 - 3.494x - 0.092x^2 + 0.048x^3 - 0.005x^4, \tag{17a}$$

$$(\alpha_z^{(2p_-)} - \alpha_z^{(1s)}) = 0.016 - 2.931y - 0.156y^2 + 0.096y^3 - 0.012y^4. \tag{17b}$$

In Eqs. (17a) and (17b) $x = \gamma^{-1.35}$ and $y = \gamma^{-1.09}$. These formulas are consistent with values tabulated in this paper to within 1%.

Similar fitting to the $1s \to 2p_0$ transitions for $0.3 \leqslant \gamma \leqslant 5.0$ leads to the interpolation formulas of Eqs. (18a) and (18b):

$$(\alpha_\perp^{(2p_0)} - \alpha_\perp^{(1s)}) = -0.118 - 3.313v - 0.632v^2 + 0.211v^3 - 0.021v^4, \tag{18a}$$

$$(\alpha_z^{(2p_0)} - \alpha_z^{(1s)}) = -5.979 - 27.761w - 3.00w^2 - 2.423w^3 + 0.222w^4. \tag{18b}$$

In Eqs. (18a) and (18b) $v = \gamma^{-0.9}$ and $w = \gamma^{-0.654}$. These formulas fit the values inferred from Tables III and IV to well within 1%.

A partial check on Tables II and III can be obtained by calculating upper and lower bounds on the magnitude of $\alpha_\perp$ and α_z. The basic inequality underlying such calculations is

$$\langle 2p|H'^2|2p\rangle = \sum_n \langle 2p|H'|n\rangle\langle n|H'|2p\rangle \geqslant |\langle m|H'|2p\rangle|^2 .$$

Thus if the lowest-energy intermediate state $|l\rangle$ lies above $|2p\rangle$ in energy then

$$\frac{|H'_{2p,l}|^2}{(E_l - E_{2p})} \leqslant \sum_n \frac{|H'_{2p,n}|^2}{E_n - E_{2p}} \leqslant \frac{\langle 2p|H'^2|2p\rangle}{(E_l - E_{2p})}. \qquad (19)$$

The inequalities of Eq. (19) are rigorous when exact unperturbed states are employed, but it can be expected that they would hold also for the quite accurate unperturbed states employed in this paper. For those perturbation sums considered here in which the 1s state occurs the inequalites can easily be modified by omitting that intermediate state from the perturbation sum and then adding its contribution back at the end of the calculation. [In that case one replaces $\langle 2p|H'^2|2p\rangle$ on the right-hand side of Eq. (19) by $\langle 2p|H'^2|2p\rangle - |\langle 1s|H'|2p\rangle|^2$.]

Surprisingly the six unperturbed functions of Eqs. (12) suffice for calculating useful bounds for the various polarizability coefficients over the range of magnetic fields considered in this paper. An example of such bounds, for $\gamma=1$, is given in Eqs. (20a)–(20d). States $|\varphi^{(A)}_{3d_{-1}}\rangle$ and $|\varphi^{(A)}_{3d_{-2}}\rangle$ defined in Eqs. (12d) and (12e) have been employed in matrix elements required for the calculation of the bounds of Eqs. (20b) and (20c) and Eq. (20a), respectively:

$$3.93 \leqslant |\alpha_\perp^{(2p_-)}| \leqslant 4.93, \qquad (20a)$$

$$3.41 \leqslant |\alpha_z^{(2p_-)}| \leqslant 3.73, \qquad (20b)$$

$$4.275 \leqslant |\alpha_\perp^{(2p_0)}| \leqslant 4.395, \qquad (20c)$$

$$39.27 \leqslant |\alpha_z^{(2p_0)}| \leqslant 40.05. \qquad (20d)$$

The tight bracketing of α indicated in Eqs. (20b) and (20c) and in Eq. (20d) is a consequence of relatively strong coupling to the $3d_{-1}$ and 2s states, respectively. The close proximity of $|\alpha_\perp^{(2p_-)}|$ to its lower bound is likewise due to strong coupling to the $3d_{-2}$ level; the large value of $|\alpha_z^{(2p_0)}|$ is mainly attributable to the small energy difference between the $2p_0$ and 2s levels.

It is evident from Tables II–IV that the magnitudes of all the polarizabilites decrease with increasing magnetic field. That is a consequence of both magnetic compression of the wave functions (arising from the term $\gamma^2\rho^2/4$ in H_0), which reduces the matrix elements of the electric field, and the increase of energy separations between levels, which increases the magnitudes of the energy denominators.

Both $\alpha_\perp^{(2p_{-1})}$ and $\alpha_z^{(2p_0)}$ diverge in the limit $\gamma\to 0$ at fixed electric field [the singularity of $\alpha_\perp^{(2p_{-1})}$ arises from the divergence of $\beta(0,1)$ in Eq. (6c)]. These divergences are caused by vanishing energy denominators associated with the degeneracy of 2p and 2s states at $\gamma=0$. However, they are unphysical and result from the use of Rayleigh-Schrodinger perturbation theory outside of its range of validity. At very weak magnetic fields where the electric field matrix elements coupling 2p states to 2s are comparable to the magnetic shifts of the unperturbed levels it is much more accurate to diagonalize directly the 4×4 Hamiltonian matrix formed from the 2s, $2p_-$, $2p_0$, and $2p_+$ basis functions. This leads to the equation

$$E = \frac{|\langle 2s|H'^{(+)}|\varphi_{2p_-}\rangle|^2}{(E+\gamma)} + \frac{|\langle 2s|H'^{(-)}|\varphi_{2p_+}\rangle|^2}{(E-\gamma)} + \frac{|\langle 2s|H'^{(z)}|\varphi_{2p_0}\rangle|^2}{(E+4\gamma^2)}, \qquad (21)$$

where E in Eq. (21) is the difference in energy between a perturbed energy and the energy of the zero-field $n=2$ states ($-\mathrm{Ry}/4$). Normalized zero-field wave functions may be used in calculating the matrix elements; only the lowest order term in γ has been retained in each energy denominator. In such weak magnetic fields, of course, the energy shifts of the levels are no longer linear in the squares of the components of the electric field vector.

TABLE V. Comparison of two calculations at $\gamma=1$ of the quantity $4\beta(0,1)$ as defined in Eq. (6c). The number of parameters in the trial wave function for the polarizability is equal to the number at the top of each column. The row entries labeled “present” are from the present calculation. The row labeled “Ref. 4” are calculated by the method of Ref. 4 (no orthogonalization to 1s) but using the wave functions of the present paper. It is expected that the “present” row gives an upper bound to $4\beta(0,1)$. (That would certainly be true if the wave functions $\varphi^{(A)}$ were exact.)

Parameters	1	2	3	4	6
Present	0.555	−0.0299	−0.1339	−0.1408	−0.1409
Ref. 4	2.55	−0.019	−0.1229	−0.1248	

Finally, it is of interest to compare the rate of convergence of calculations with and without orthogonalization of the trial function Ψ to the 1s state. In the present paper such orthogonalization is made, whereas it is omitted in the method of Ref. 4. To this end a sequence of trial functions for $\Psi^{(3)}$ in Eq. (13c) is employed for the approximate evaluation of $\beta(0,1)$ defined in Eq. (6c). These trial functions are, in turn, defined by Eq. (13c). Consider the ordered parameter list given below.

$$(a_0, a_1, b_0, b_1, a_2, c_0).$$

An n-parameter trial function is defined as a function given by Eq. (13c) such that the first n parameters of the list are optimized and all other parameters fixed at zero. (Thus, for example, a three-parameter wave function will employ only the parameters a_0, a_1, and b_0.) It is to be hoped that the value obtained for $\beta(0,1)$ will converge rapidly with increasing number of optimized parameters. A comparison of the convergence for $\gamma=1$ is given in Table V. It appears that orthogonalization speeds convergence. Similar results are obtained at other values of γ.

III. CONCLUSION

Calculations of the polarizability of a hydrogen atom in its $1s$, $2p_-$ and $2p_0$ states for electric fields parallel and perpendicular to an applied magnetic field are formulated as energy minimization problems, which are solved variationally. The results are tabulated over a range of dimensionless magnetic field, γ, between 0.3 and 5.0. Interpolation formulas are displayed which are expected to enable calculation of quadratic Stark effect shifts of magneto-optical transitions $1s \rightarrow 2p_-$ and $1s \rightarrow 2p_0$ in weak electric fields to an accuracy of approximately 1%.

---

[1] D. M. Larsen, Phys. Rev. B **8**, 535 (1973).

[2] D. M. Korn and D. M. Larsen, Solid State Commun. **13**, 807 (1973).

[3] D. M. Larsen, Phys. Rev. B **25**, 1126 (1982).

[4] P. A. Fedders, Phys. Rev. B **27**, 4799 (1983).

[5] H. C. Praddaude, Phys. Rev. A **6**, 1321 (1972).

[6] Yu. P. Kravchenko, M. A. Liberman, and B. Johansson. Phys. Rev. A **54**, 287 (1996).