

Exact solutions for perturbed confined hydrogen atoms: Polarizabilities and nuclear shielding factors

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We extend our recent treatment of a well-known model of a nonrelativistic hydrogen-like atom confined within an impenetrable spherical “box” of radius R . Analytical closed-form solutions are presented for the first-order perturbation corrections appropriate to the dipole polarization of *all* s states. *Exact* solutions are expressed conveniently in terms of Kummer (confluent hypergeometric) M functions, exactly as for the field-free atom, by exploiting several well-known recurrence and differential relations for these functions. The M functions and all necessary integrals are evaluated using standard MAPLE routines, which exploit analytical properties of these functions. The accuracy of our procedures has been checked by a similar calculation of the dipole shielding factors. Our procedures are easily extended to states of nonzero angular momentum, as well as to higher-multipole perturbations. Our exact values may be of interest in assessing the utility of this simple model of atomic confinement.

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I. INTRODUCTION

The concept of a confined system was originally suggested by Michels *et al.* [1] and applied to an astrophysical problem by Sommerfeld and Welker [2] who used the model of a confined hydrogen atom in a spherical box. The model of a confined system has been used extensively for many years in such diverse fields as the effect of pressure on energy levels, the cell model of the liquid state, semiconductor quantum dots, and problems in astrophysics, such as the rate of escape of stars from galactic clusters and the theory of white dwarfs. An extensive list of references to many applications may be found in Varshni [3] who treats the problem of confined hydrogen approximately.

Our present interest centers on the effect of an applied field on confined hydrogenlike systems and in particular on finding *exact* solutions for the first-order equation for treating such a field perturbatively. The analytical function obtained is used to calculate polarizabilities and nuclear shielding factors. Recently (Burrows and Cohen [4]), we used a mixture of Lie algebraic and analytical methods to obtain closed-form solutions of a model for a *confined hydrogenlike atom* (CHA) of nuclear charge Z . The model Hamiltonian (in conventional atomic units) is

$$H_0 = -\frac{1}{2}\nabla^2 + V_0(r|R), \quad (1)$$

$$V_0(r|R) = \begin{cases} -\frac{Z}{r}, & 0 \leq r < R, \\ \infty, & r \geq R, \end{cases} \quad (2)$$

and so differs from the usual *unconfined hydrogenlike atom* (UHA) only in that a radial boundary condition must be satisfied at a *finite radius* $r=R$ (of the supposedly impenetrable barrier), instead of at infinite R . This model has attracted a large variety of calculations over the years and still serves as a generic model for studies of possible pressure effects on general atoms. Quite recently, we gave both approximate (Laughlin *et al.* [5]) and exact [4] solutions of the field-free problem, and it is clearly preferable to employ exact solutions in order to investigate properties other than the energies of the model. In the present work, we obtain analytical solutions of the first-order equations appropriate to the dipole polarization of *all* s states of the CHA. These may be seen as a generalization of the analytical solutions for the multiple polarizabilities of the ground state of the UHA (Dalgarno and Lewis [6]), and we have calculated both polarizabilities and shielding factors (cf. Dalgarno [7]) for the CHA ground state over a range of confinement radii R . The zeroth-order solutions for a general (nl) state are written very conveniently as a product of a simple harmonic function (a solution of Laplace's equation) and a purely radial function (since angular momentum remains quantized, exactly as for the UHA):

$$\psi_0 = Nr^l Y_{lm}(\theta, \phi) \exp(-x/2) M(c, d, x), \quad E_0 = -\frac{1}{2}\alpha^2. \quad (3)$$

Here, N is a normalization constant, Y_{lm} is the usual spherical harmonic, the parameter α (different for each state) must be determined numerically from a zero of the Kummer M function $M(c, d, x)$ at $r=R$ so as to satisfy the required boundary condition, while the scaled radius x and the parameter c both depend explicitly on α ; we write

$$c = (l+1) - \frac{Z}{\alpha}, \quad d = 2(l+1), \quad x = 2ar. \quad (4)$$

Note that, in the UHA limit as $R \rightarrow \infty$, it is found that

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$$\alpha \rightarrow Z/(n+l+1), \quad c \rightarrow -n, \quad (5)$$

so that the Kummer M functions become Laguerre polynomials and we recover the conventional solutions.

The calculation of α for each confinement radius R and for each nl state has been achieved fairly easily using standard MAPLE packages for locating the zeros of the M functions. This is not a completely trivial exercise, which we will address briefly in the Appendix.

In the present work, we treat in detail the dipole polarizabilities and shielding factors of a general ns state of the CHA. Our numerical results for the ground-state polarizabilities confirm and improve some recent numerical calculations (Montgomery [8], Laughlin [9]), and our solutions are given in closed form in terms of finite sets of M functions and their derivatives, all of which may be calculated using MAPLE. These *exact* solutions are new, and it is clear that our procedures may be generalized to treat *all* nl states, as well as other (higher-order) polarizabilities and shielding factors, which we do not consider here.

The nonrelativistic quantum mechanical formulas for the dipole polarizability and shielding factor of a one-electron atom with field-free normalized wave function ψ_0 and first-order correction ψ_1 are given by [7]

$$\alpha_d = 2\langle \psi_1 | r \cos(\theta) | \psi_0 \rangle, \quad (6)$$

$$\beta_d = 2\langle \psi_1 | \frac{1}{r^2} \cos(\theta) | \psi_0 \rangle, \quad (7)$$

where the first-order solution ψ_1 satisfies the inhomogeneous equation

$$(H_0 - E_0)\psi_1 = -[r \cos(\theta)]\psi_0. \quad (8)$$

Note that Eq. (8) is *not* an eigenvalue problem and, on account of the angular factor in ψ_0 , there is no first-order energy shift for *any* state of the CHA.

An equivalent expression for the dipole shielding factor is

$$\beta_d = 2\langle \psi'_1 | r \cos(\theta) | \psi_0 \rangle, \quad (9)$$

where ψ'_1 satisfies the analog of Eq. (8),

$$(H_0 - E_0)\psi'_1 = -\left(\frac{1}{r^2} \cos(\theta)\right)\psi_0. \quad (10)$$

The derivation of Eq. (9) depends on the operator $H_0 - E_0$ being Hermitian, which in turn relies on the boundary conditions. We require the total wave function to vanish at $r = R$ (to all orders); thus, it is necessary to ensure that all of the wave functions ψ_0 , ψ_1 , and ψ'_1 vanish at $r = R$. In the following section we give a detailed derivation of the solution ψ_1 , making extensive use of several known recurrence, derivative, and numerical properties of these M functions (we follow the notations of Abramowitz and Stegun [10] and label their equations with AS). Apart from any intrinsic interest, the calculation of shielding factors using *both* Eqs. (7) and (9) provides an *independent* check on the accuracy of the entire calculation. This check is particularly valuable, as we are unaware of any earlier calculation of shielding factors for comparison (except for the limiting case of the UHA). Our

calculated polarizabilities serve to improve and confirm some recent sets of numerical calculations [5,6].

II. ANALYTICAL SOLUTIONS FOR THE CHA

A. Field-free solutions

Here, we give a brief (purely analytical) derivation of the zeroth-order solutions of the CHA; similar procedures are used to solve Eqs. (8) and (10) below.

The field-free Schrödinger equation is first multiplied by $-2r$:

$$-2r(H_0 - E_0)\psi_0 = 0. \quad (11)$$

On account of the confinement caused by the impenetrable barrier at $r = R$, all states of the CHA are *bound* states. We now express the solutions ψ_0 in product form (but note carefully that this is *not* the usual complete separation of variables and the motivation for our approach has been given in Burrows and Cohen [4])

$$\psi_0 = r^l Y_{lm}(\theta, \phi) \chi(r). \quad (12)$$

The purely radial factor $\chi(r)$ then satisfies the equation

$$[rD_r^2 + 2(l+1)D_r + 2Z + 2E_0r]\chi = 0, \quad \chi(R) = 0, \quad D_r = \frac{d}{dr}. \quad (13)$$

Introducing a *scale parameter* α , writing $x = 2\alpha r$, and

$$\chi(r) = \exp(-x/2)y(x), \quad (14)$$

it is readily found that α may be chosen so that

$$E_0 = -\frac{\alpha^2}{2} \quad (15)$$

and the function $y(x)$ satisfies the ordinary differential equation

$$L(c, d, x)y(x) = [xD^2 + (d-x)D - c]y(x) = 0, \quad D = \frac{d}{dx}, \quad (16)$$

where the parameters c and d are given by

$$c = (l+1) - \frac{Z}{\alpha}, \quad d = 2(l+1). \quad (17)$$

Equation (16) is the canonical Kummer equation (AS-13.1.1), with one convergent series solution (regular at $x=0$) denoted by

$$y(x) = M(c, d, x), \quad (18)$$

and to satisfy the boundary conditions, we require $M(c, d, 2\alpha R) = 0$. Thus, the complete solution for any given pair (R, l) is achieved by locating successive zeros of $M(c, d, x)$ as a function of α ; this has been achieved using standard MAPLE computing packages. We note that, although both c and x depend on α , this presents no difficulty. Once α has been computed in this way, the corresponding field-free

energy is calculated from Eq. (15), while the complete solution ψ_0 is normalized so that

$$\langle \psi_0 | \psi_0 \rangle_R = 1, \quad (19)$$

where the subscript R in Eq. (19) denotes that the radial part of this three-dimensional integral is to be taken over the finite range $0 \leq r \leq R$. This completes our derivation of the solution ψ_0 given in Eq. (3) above.

B. First-order solutions for s states

For simplicity of presentation, we now treat in detail only the solution of Eq. (8) appropriate to the case of the dipole polarizability of a general ns state of the CHA placed in a uniform field in the z direction. The necessary extensions to other field directions, to other states, and to higher-multipole polarizabilities are all straightforward and will not be pursued here. We give an outline of the corresponding solution of Eq. (10), appropriate to shielding factors, in the following subsection.

As before, we first multiply Eq. (8) throughout by $-2r$, so that we actually treat the equation

$$-2r(H_0 - E_0)\psi_1 = 2r[r \cos(\theta)]\psi_0 \quad (20)$$

and we solve Eq. (20) over $0 < r < R$ subject to the same boundary condition on $r=R$ so that $\psi_1(R) = \psi_0(R) = 0$. Now, for any unperturbed ns state (with $l=0$), we have a purely radial solution for ψ_0 ,

$$\psi_0 = N \exp(-x/2)M(c, d, x), \quad (21)$$

and we observe that the presence of the factor $r \cos(\theta)$ on the right-hand side of Eq. (20) implies that we may write the perturbed solution ψ_1 of any s state in a form analogous to a field-free p state solution (with $l=1$) of Eq. (11) above:

$$\psi_1 = Nr \cos(\theta) \exp(-x/2)F(x). \quad (22)$$

In ψ_1 we use the same values of α , N , and x as in ψ_0 and E_0 is similarly unchanged; thus, substituting Eqs. (21) and (22) into Eq. (20) leads to the following equation for $F(x)$:

$$L(c+1, d+2, x)F(x) = \mu x M(c, d, x),$$

$$\mu = \frac{1}{2\alpha^2}, \quad c = 1 - \frac{Z}{\alpha}, \quad d = 2. \quad (23)$$

The new parameters $(c+1, d+2)$ on the left-hand side of Eq. (23) both arise from the p -state character of the solution ψ_1 (with $l=1$) by comparison with the s -state character of ψ_0 .

In order to obtain the solution of Eq. (23) satisfying the boundary condition at $r=R$ we also need to solve the homogeneous equation

$$L(c+1, d+2, x)f(x) = 0. \quad (24)$$

Its solution is simply $f(x) = M(c+1, d+2, x)$, and the complete solution of Eq. (23) may then be formed from $f(x)$ and any particular solution. We construct such a particular solution as follows.

It is easily verified [using the definition of the operator $L(a, b, x)$ and Kummer's equation] that for any k which differs from a ,

$$L(a, b, x)M(k, b, x) = (k-a)M(k, b, x), \quad (25)$$

while, taking the partial derivative of Kummer's equation for $M(a, b, x)$ with respect to the parameter a ,

$$\frac{\partial}{\partial a}[L(a, b, x)M(a, b, x)] = L(a, b, x)\frac{\partial}{\partial a}[M(a, b, x)] - M(a, b, x) = 0. \quad (26)$$

Thus we can always find a particular solution of a general inhomogeneous equation of the form

$$L(a, b, x)F_p(x) = G(x) \quad (27)$$

in terms of Kummer functions *provided only* that $G(x)$ can be expressed as a superposition of the set of functions $\{M(k, b, x)\}$ with *fixed* b . To solve Eq. (23), we need only calculate the expansion coefficients A_k in the expansion

$$xM(c, d, x) = \sum_k A_k M(c-1+k, d+2, x). \quad (28)$$

In order to establish Eq. (28) we use (AS-13.4.1) with c, d replacing a, b ,

$$xM(c, d, x) = (c-d)M(c-1, d, x) + (d-2c)M(c, d, x) + cM(c+1, d, x), \quad (29)$$

together with repeated application of (AS-13.4.3), leading to

$$d(d+1)M(k, d, x) = (d-k)(d+1-k)M(k, d+2, x) + 2k(d-k)M(k+1, d+2, x) + k(k+1)M(k+2, d+2, x). \quad (30)$$

The coefficients A_k in Eq. (27) are then calculated explicitly (with $d=2$):

$$A_0 = \frac{(c-2)(c-3)(c-4)}{6},$$

$$A_1 = -2 \frac{(c-1)(c-2)(c-3)}{3},$$

$$A_2 = c(c-1)(c-2),$$

$$A_3 = -2 \frac{(c+1)c(c-1)}{3},$$

$$A_4 = \frac{(c+2)(c+1)c}{6}. \quad (31)$$

Then the required particular solution of Eq. (23) is given by

$$F_p(x) = \mu \left\{ -\frac{1}{2}A_0M(c-1,4,x) - A_1M(c,4,x) + A_2\frac{\partial}{\partial c}M(c+1,4,x) + A_3M(c+2,4,x) + \frac{1}{2}A_4M(c+3,4,x) \right\}, \quad (32)$$

and the complete solution, which also satisfies the boundary condition $F(\tau)=0$ where $\tau=2\alpha R$, may be written conveniently

$$F(x) = F_p(x) - F_p(\tau)\frac{M(c+1,4,x)}{M(c+1,4,\tau)}. \quad (33)$$

This completes the solution for ψ_1 , and using it together with ψ_0 we may now calculate both the polarizabilities and shielding factors from Eqs. (6) and (7). It is readily seen that the three-dimensional matrix element which appears in Eq. (6) reduces, after integrations over the angles θ and ϕ , to a purely radial integral (over the *finite range* $0 < r < R$)

$$\frac{8\pi}{3}N^2 \int_0^R \exp(-r)r^4M(c,2,2\alpha r)F(2\alpha r)dr, \quad (34)$$

while the normalization integral of ψ_0 determines N^2 from

$$1 = 4\pi N^2 \int_0^R \exp(-r)r^2[M(c,2,2\alpha r)]^2dr. \quad (35)$$

Thus, the numerical evaluation of α_d is reduced to quotients of integrals over Kummer functions for which the numerical evaluation is straightforward (see below); a similar result holds for β_d .

C. Additional solution

Comparing Eqs. (8) and (10), we note that the only change is to replace one factor on the right-hand side, $r \cos(\theta)$, by $(1/r^2)\cos(\theta)$. Since both are harmonic functions, we now follow exactly the same procedure as before and adopt the form

$$\psi_1' = N\frac{1}{r^2} \cos(\theta)\exp(-x/2)G(x). \quad (36)$$

The resulting inhomogeneous equation for $G(x)$ differs from that for $F(x)$ in Eq. (23) *only* in having the operator $L(c-2, d-4, x)$ in place of $L(c+1, d+2, x)$:

$$L(c-2, d-4, x)G(x) = \mu xM(c, d, x). \quad (37)$$

[Quite generally, in calculating multipole effects—when $r^l P_{lm}$ is to be replaced by $(1/r^{l+1})P_{lm}$ —the corresponding change to the radial equation is simply to replace $l \rightarrow -(l+1)$.]

Since the second parameter value on the left-hand side of Eq. (37) is now smaller than that on the right-hand side, we require a different strategy for this problem from our earlier solution of Eq. (22). Here we note a generalization of Eq. (25):

$$L(a, b, x)M(k, m, x) = \frac{k}{m}(b-m)M(k+1, m+1, x) + (k-a)M(k, m, x). \quad (38)$$

This uses the definitions of $L(a, b, x)$ and $M(k, m, x)$ as well as the general differential property (AS-13.4.8):

$$DM(k, m, x) = \frac{k}{m}M(k+1, m+1, x). \quad (39)$$

In this case we may express $xM(c, 2, x)$ both in the form derived from Eq. (29) (with $d=2$) and also [using (AS-13.4.4)]

$$xM(c, 2, x) = M(c, 1, x) - M(c-1, 1, x), \quad (40)$$

and we now seek a particular integral of Eq. (37) of the form

$$G(x) = \mu \sum_{k=0}^2 B_k M(c-2+k, 1, x), \quad (41)$$

since from Eq. (36) we see that

$$L(c-2, -2, x)M(k, 1, x) = (k+2-c)M(k, 1, x) - 3kM(k+1, 2, x). \quad (42)$$

By inspection, we have a particular integral

$$G_p(x) = -\mu\{M(c-2, 1, x) - 2M(c-1, 1, x) + M(c, 1, x)\}, \quad (43)$$

so that the formal solution which satisfies the boundary condition is

$$G(x) = G_p(x) - G_p(\tau)\frac{x^3M(c+1, 4, x)}{\tau^3M(c+1, 4, \tau)}. \quad (44)$$

Note that it is necessary to use the alternative solution to the Kummer equation $x^{1-b}M(1+a-b, 2-b, x)$ (AS-13.1.13) since in general $M(c-1, -2, x)$ is not defined.

III. RESULTS FOR THE GROUND STATE

The results of our calculations of dipole polarizabilities and nuclear shielding factors of the ground $1s$ state of the CHA are presented in Tables I and II. Table I includes results of some earlier precise polarizability calculations (Montgomery [8], Laughlin [9]); all values are in complete agreement, and we have now listed values which are certainly correct to at least eight significant decimal digits over the entire range of confinement radii R . This accuracy is certainly sufficient for most physical applications.

Table II gives similar results for the shielding factors, calculated with both ψ_1 and ψ_1' for the same range of R values. These are also identical to at least eight significant decimal digits. We have not discovered any earlier accurate calculations of shielding factors.

We emphasize that similar calculations may obviously be carried through for other (excited) s states, and it is to be expected that similar high accuracy can be expected for such states; our methods can be extended straightforwardly to un-

TABLE I. Polarizabilities.

R	$\alpha_d (h=0.001)$	α_d (Laughlin)	α_d (Montgomery)
∞	4.5	4.5	4.5
10	4.49681418	4.496814	4.49681
8	4.45396472	4.453965	4.45396
6	4.05814050	4.058140	4.05814
4	2.37798233	2.377982	2.37798
2	0.342558111	0.342558	0.34256
1	0.0287920226	0.028792	0.02879
0.5	0.00203563840	—	—
0.25	0.000134604036	—	—
0.125	0.00000864270980	—	—

TABLE II. Nuclear shielding factors.

R	$\beta_d (h=0.001)$	β_d (additional)
∞	1	1
10	0.999957586	0.999957586
8	0.999131573	0.999131573
6	0.987274170	0.987274170
4	0.894473120	0.894473121
2	0.572902117	0.572902116
1	0.312211770	0.312211769
0.5	0.161660577	0.161660577
0.25	0.0821146022	0.0821146022
0.125	0.0413659810	0.0413659810

perturbed states of nonzero angular momentum without difficulty.

This calculation illustrates that the exact solutions found may easily be used in quadrature calculations to obtain accurate estimates of the polarizabilities and nuclear shielding factors. In the following appendix, we include some details of the numerical methods employed in the present work. It would appear that standard MAPLE packages are extremely reliable for calculations with Kummer M functions.

APPENDIX: NUMERICAL PROCEDURES

All the numerical procedures used in this paper depend ultimately on the evaluation of the Kummer M functions $M(a, d, x)$ with prescribed sets of values of $a, d,$ and x ; the derivatives $\partial M/\partial a$ and $\partial M/\partial x$ are also evaluated from other M functions. In Ref. [10] (p. 511) there is a comprehensive section on numerical methods which mainly depend on the recurrence relations such as

$$d(a+x)M(a, d, x) + x(a-d)M(a, d+1, x) - adM(a+1, d, x) = 0 \tag{A1}$$

[(AS-13.4.5)] and transformations such as

$$M(a, d, x) = e^x M(d-a, d, -x) \tag{A2}$$

[(AS-13.1.27)]. In the present work we have used the computer package MAPLE which evaluates $M(a, d, x)$ accurately and efficiently.

However, for each state considered and for each specified confinement radius R , it is first necessary to determine a parameter α *once only* from the appropriate zero of

$$M(1-z/\alpha, 2, 2\alpha R) = 0. \tag{A3}$$

Any standard root-finding process may be used here; in the cases where α is imaginary ($E_0 > 0$), it is more convenient to solve the real equation

$$|M(1-z/\alpha, 2, 2\alpha R)|^2 = 0 \tag{A4}$$

and the same techniques may be employed.

The numerical integration is straightforward since integrands contain only standard functions (including the Kummer M functions), and these can all be evaluated to the full precision used. However, we also need to consider carefully the calculation of

$$\frac{\partial}{\partial a} M(a, d, x), \tag{A5}$$

which is required for F_p in Eq. (32) above. We have used a finite-difference approximation with fourth-order error so that

$$\exp\left(-\frac{x}{2}\right) \frac{\partial}{\partial a} M(a, d, x) \approx \Delta(h, x), \tag{A6}$$

where $\exp(x/2)\Delta(h, x)$ is given by

$$\frac{M(a-2h, d, x) - 8M(a-h, d, x) + 8M(a+h, d, x) - M(a+2h, d, x)}{12h}. \tag{A7}$$

This particular form of $\Delta(h, x)$, which includes the exponential asymptotic factor, has been found useful for the cases where R is large.

The routines in MAPLE have been used without adaption

for all values of R except $R=2$, and the results are obtained accurately and speedily using 12-digit precision. In the case $R=2$, where $a=0$ in (A7), the unadapted method leads to longer computations to achieve an accuracy consistent to 12

significant figures. In such a situation we may reverse the order of the calculations so that instead of the computation of integrals such as

$$\int_0^2 \Delta(h, 2\alpha r) \psi_0(2\alpha r) r^4 dr, \quad (\text{A8})$$

we use

$$\frac{1}{24h} \sum_{j=1}^4 I_j,$$

$$I_1 = 2 \int_0^2 M(a - 2h, d, 2\alpha r) \psi_0(2\alpha r) r^4 \exp(-\alpha r) dr,$$

$$I_2 = -16 \int_0^2 M(a - h, d, 2\alpha r) \psi_0(2\alpha r) r^4 \exp(-\alpha r) dr,$$

$$I_3 = 16 \int_0^2 M(a + h, d, 2\alpha r) \psi_0(2\alpha r) r^4 \exp(-\alpha r) dr,$$

$$I_4 = -2 \int_0^2 M(a + 2h, d, 2\alpha r) \psi_0(2\alpha r) r^4 \exp(-\alpha r) dr. \quad (\text{A9})$$

In this way the computational error is essentially the error in numerical integration and h can be chosen sufficiently small to obtain consistent results. This procedure enables accurate results for the case $R=2$ to be obtained quickly even though the computation of one integral has been replaced by estimates for four integrals. All results of this work presented in Tables I and II were calculated with $h=0.01$ and $h=0.001$, with identical values for *all* significant digits.

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