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Higher Rydberg states of He using the polarized-orbital method

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Rydberg states of He of the configuration $(1s\,nl)\,{}^{1,3}D$, ${}^{1,3}F$ for $n = 3$–7 have been calculated using polarized-orbital and related approximations, notably the extended-polarization approximation. The singlet states are superior in the full polarized-orbital approximation whereas the triplet cases are better in the extended-polarization approximation. Reasons for this behavior are given. Comparison is also made with recent diagrammatic calculations of Chang and Poe. A comment on some recent polarized-orbital calculations of photoionization is included.

Because bound-state energies are more accurately determinable experimentally than scattering parameters, they provide a more exacting test of calculational theories. An example is in the case of He where very accurate measurements by Wing and Lamb have recently been made.[1] Actually these microwave-optical measurements are particularly suited to energy differences, whereas we are primarily interested in the energies of the individual states. A recent compilation of these data has been given by Martin[2] and it is those data to which we shall compare our results on the $(1s,nl)$ states of helium. We are not interested in very high n, because at that point a simple quantum-defect formula is applicable with $\mu = \mu(\infty)$, and the deviation of the experimental and theoretical values of $\mu(\infty)$ is all that the comparison affords.

The theories which we wish to compare are basically polarized-orbital[3,4] and extended-polarization[5] approximations. In both theories the outer electron is described by the bound counterpart of a scattered orbital, $u_n(r)$, satisfying an equation of the form (in Ry units, throughout)

$$\left(\frac{d^2}{dr^2} + \frac{2(z-1)}{r} + 2e^{-2zr}(z+1/r) - \frac{l(l+1)}{r^2} + V(r) + \epsilon_n\right)u_n(r) = O\,u_n\,. \quad (1)$$

The left-hand side of this equation includes the Hartree potential for nuclear charge z ($z=2$ in this application), the centrifugal barrier $-l(l+1)/r^2$, and a distortion potential $V(r)$, where for the two approximations we shall consider

$$\begin{aligned} V(r) &= \alpha(r)/r^4, && \text{polarized orbital;} \\ &= V_p(r) + V_d(r), && \text{extended polarization.} \end{aligned} \quad (2)$$

$\alpha(r)/r^4$ and $V_p(r)$ are different forms of the first-order adiabatic polarization potential, both of which approach α/r^4 as $r \to \infty$, where α is the polarizability of the target, $\alpha = 4.5/z^4$. $V_d(r)$ is the nonadiabatic distortion potential appropriate to the extended-polarization approximation.[5] In the present calculation, $V_p + V_d$ has been kindly supplied by Drachman in numerical form from an exact evaluation in spheroidal coordinates[6] rather than as a relative partial-wave expansion as done by Callaway *et al.*[5]

The bound nature of the problem is reflected in the fact that ϵ_n is an eigenvalue which is related to the total energy E_n by

$$E_n = -z^2 + \epsilon_n\,. \quad (3)$$

In practice we solve for ϵ_n by perturbation theory whereby if $u_n^{(0)}$ and $\epsilon_n^{(0)}$ are the eigenfunction and eigenvalue obtained by setting the right-hand side of (1) equal to zero, then letting

$$\epsilon_n = \epsilon_n^{(0)} + \Delta\epsilon_n\,, \quad (4)$$

it follows rather trivially to first order that

$$\Delta\epsilon_n = \int_0^\infty u_n^{(0)} O\, u_n^{(0)}\, dr \Big/ \int_0^\infty [u_n^{(0)}(r)]^2\, dr. \quad (5)$$

The right-hand side of (1) includes in all cases the exchange terms plus the exchange-polarization terms in the case of the polarized-orbital method[4,7]:

$$\begin{aligned} O u_n^{(0)} &= \int_0^\infty [V_{\text{ex}}(r,r') + V_{\text{ex-pol}}(r,r')]\, u_n^{(0)}(r')\, dr', && \text{polarized orbital;} \\ &= \int_0^\infty V_{\text{ex}}(r,r')\, u_n^{(0)}(r')\, dr', && \text{extended polarization.} \end{aligned} \quad (6)$$

TABLE I. $\epsilon_n + 1/n^2$ for the ($1s\,nl$) states of He (in units of 10^{-6} Ry).

Symmetry	n	Exchange approximation	Exchange adiabatic	Polarized orbital	Extended polarization	Diagrammatic[a]	Expt.[b]
^1D	3	+19.2	−123.0	−127.2	−110.1	−126.8	−130.5
	4	+11.1	−54.9	−57.4	−47.9	−56.3	−59.7
	5	+6.4	−28.8	−30.2	−24.8	−31.0	−31.7
	6	+3.9	−16.9	−17.7	−14.4	−18.3	−18.7
	7	+2.6	−10.7	−11.2	−9.1	−11.7	−11.9
^3D	3	−32.9	−177.2	−173.0	−163.7	−157.6	−161.6
	4	−19.1	−86.3	−83.9	−79.0	−76.1	−77.7
	5	−11.1	−47.0	−45.5	−42.8	−41.3	−42.1
	6	−6.8	−28.0	−27.1	−25.5	−24.7	−25.0
	7	−4.4	−17.9	−17.4	−16.3	−15.8	−16.3
^1F	4	0	−10.4	−10.4	−10.2	−9.7	−10.2
	5	0	−6.0	−6.0	−5.8	−5.6	−6.2
	6	−0.0	−3.6	−3.6	−3.5	−3.5	−3.8
	7	+0.1	−2.3	−2.3	−2.3	−2.3	−2.3
^3F	4	−0.1	−10.5	−10.5	−10.3	−9.9	−10.3
	5	−0.1	−6.0	−6.0	−5.9	−5.7	−6.2
	6	−0.0	−3.7	−3.7	−3.6	−3.5	−3.9
	7	−0.0	−2.4	−2.4	−2.3	−2.3	−2.3

[a] T. N. Chang and R. T. Poe, Ref. 8.

[b] W. C. Martin, Ref. 2.

(We have checked the perturbation theory with full solutions in the exchange approximation and have found satisfactory agreement; thus we are confident that perturbation treatment is adequate for the purposes of the present comparison.)

The numerical aspects of this calculation were quite simple. A binary search was used to locate $\epsilon_n^{(0)}$, and the calculation of $\Delta\epsilon_n$ requires a straightforward numerical quadrature. Results for some relevant cases are given in Table I. In addition to the two main approximations we have given the two subsidiary approximations to the method of polarized orbital: (i) the exchange approximation, wherein we neglect the $V(r)$ term on the left-hand side of Eq. (1) and $V_{\text{ex-pol}}$ in Eq. (6) and (ii) the exchange-adiabatic approximation wherein only $V_{\text{ex-pol}}$ is neglected.

Table I shows that the exchange approximation is poor, whereas results of the exchange-adiabatic approximation are quite satisfactory. This means that the long-range static polarization potential, α/r^4, provides the main part of the correction. Corrections beyond that are all relatively small. Nevertheless where the polarized-orbital approximation yields such differences from the exchange-adiabatic results, they are always correct in sign and improve the agreement with experiment. Furthermore both polarized-orbital and exchange-adiabatic approximations are more accurate than extended-polarization results in the singlet cases whereas the latter is on the whole more accurate for triplet levels. The reasons for this are that the polarized-orbital approximation, because it arises from an ansatz for the total wave function which preserves the correct exchange symmetry, forces the outer orbital, in an approximate way, to behave reasonably where the electrons can get close together; no such provision is incorporated in the extended-polarization approximation. On the other hand, the latter correctly includes beyond the α/r^4 (static polarization potential) all of the correct r^{-6} potentials. Thus where the electrons are excluded from being together (as they are here in the triplet case) this residual long-range potential provides the dominant correction, in which case the extended-polarization approximation does better.

We have also included recent Brueckner-Goldstone diagrammatic results of Chang and Poe[8] in column 7. They are seen to be of intermediate accuracy to the other approximations for D states and of slightly poorer accuracy for F states. Of particular note with regard to the diagrammatic results is the fact that they yield singlet-triplet energy differences more accurately than the polarized-orbital approximation which in turn gives better energy differences than extended polarization.

Returning to the polarization approximations as they apply here and to low-energy phase-shift calculations, we can say that the researcher has some latitude in the choice of a suitable method.

(A more extensive comparison of phase shifts is given in our recent review article.[9]) There is another circumstance, however, which we wish to emphasize in comparing the two methods. Very often the scattering calculation is used to generate a wave function which is then used to calculate a matrix element corresponding to a different physical process, photoionization for example. In this sense we believe the polarized-orbital method provides a clear advantage. For it derives from a completely well-defined ansatz for the total wave function with correct exchange symmetry. Thus, even if one solves the polarized-orbital equations in a lesser approximation, there is still an unambiguous definition of the total wave function for further calculation. The second important point is that the form of cut-off of the polarized part of that wave function[4] provides a rapid exclusion of the polarization term where the physics of its derivation (i.e., the adiabatic approximation) no longer is applicable. In that case the wave function reduces effectively to the variational-exchange-approximate form, and this is well-known to provide a much safer approximation for the calculation of matrix elements.

Although these points have to some extent been made,[9] we restress them here because a recent "polarized-orbital" calculation of photoionization of Na and K concludes that results are sufficiently unsatisfactory to cast doubt on the validity of the method.[10] Leaving aside whether even the results warrant such a conclusion (we believe they do not), we wish to emphasize that the calculation was done in a manner quite contrary to what we have defined above and elsewhere to be used in the method of polarized orbitals. In particular this means use, in Ref. 10, of the Bethe-Reeh polarized orbital, which does not vanish for values of the scattered-particle's coordinate less than the orbital-particle's coordinate. A previous calculation[11] used the same approach in calculating Li photoionization with what was considered there to give satisfactory results. A detailed comparison with the recent and best diagrammatic calculation,[12] however, reveals unsatisfactory dissimilarities for which we believe the Bethe-Reeh polarization term is also primarily responsible. In our opinion both calculations need to be redone in the manner we have suggested. In the meantime we believe the negative comments of Ref. 10 are very misleading.

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