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Theoretical study of helium Rydberg states*

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A detailed theoretical investigation of the helium atomic Rydberg states is carried out. Results for level transition energies and doublet level splittings are found to agree extremely well with the recent high-precision microwave-optical experiments. The physical effects contributing to the electrostatic fine structures are systematically studied.

I. INTRODUCTION

The physics of atomic Rydberg states has long been the subject of experimental study with conventional spectroscopic methods.[1] The resolving power of this approach, however, has often proved to be less than adequate. Recently, a 10^4-fold improvement in resolution was achieved by Lamb and co-workers[2] (WLL) with the development of a microwave-optical technique. This experimental breakthrough enables one for the first time to study with high accuracy the electrostatic fine structure of the atomic Rydberg states such as the level shifts and level splittings. The experimental breakthrough has also added great impetus to the search for a general, first-principles theoretical approach, capable of improved quantitative predictions as well as qualitative interpretations. As emphasized by those authors,[2] the physics of the atomic Rydberg states holds special theoretical interest not only because of its quasi-hydrogenic nature but also because of its close relation to the scattering of slow electrons by the charged ion core. In this paper, we report a detailed theoretical study on the Rydberg series for atomic helium[3] within the framework of the Brueckner-Goldstone[4] (BG) perturbation-theory approach.

The BG perturbation theory was developed in the context of nuclear many-body problems, and in recent years has also been extensively applied to complex atomic and molecular[5] problems where possible many-body effects have been explored. Thus it is important at this very outset to make clear that, since the present case involved only two orbital electrons, the "many-body" aspect of the BG theory does not really enter into the problem. Rather, the BG formalism is used here because of its associated operational advantages. These include, through the graphical representation of terms or diagrams, a systematic enumeration of contributing perturbation terms and the convenience in the interpretation of the contributing physical processes involved. These aside, there is no essential difference between the present formalism and the conventional perturbation approaches.

In Sec. II, we shall briefly recall some of the essential elements of the general BG formulation. Specific details of the application to the helium $(1s, nl)$ Rydberg states as well as the physical interpretations of the contributing terms are given in Sec. III. Results and discussions of the present calculations are given in Sec. IV.

II. REVIEW OF THE BG PERTURBATION APPROACH

The first and foremost task in the BG approach, as in all perturbational approaches, is the separation of the total Hamiltonian H of the system into an "unperturbed" part H_0 and the "perturbing" part H'. For an atomic system, the total Hamiltonian consists of the single-particle operators T_i, the sum of the kinetic-energy operator K_i and the nuclear Coulomb potential operator V_i^N for the ith electron, and the Coulomb interactions ν_{ij} between the ith and the jth electrons. The most general way for the separation of H_0 and H' is through the introduction of an arbitrary (Hermitian) single-particle potential V_i:

$$\begin{aligned} H &= \sum_i (K_i + V_i^N) + \sum_{i<j} \nu_{ij} \\ &= \sum_i T_i + \sum_{i<j} \nu_{ij} \\ &= \sum_i (T_i + V_i) + \Big(\sum_{i<j} \nu_{ij} - \sum_i V_i \Big) \\ &= H_0 + H' . \end{aligned} \tag{1}$$

With a given choice of V, one generates a complete set of single-particle states ϕ_n's:

$$(T_i + V_i)\phi_n = \epsilon_n \phi_n \tag{2}$$

which in turn shall form the basis set for the perturbation expansion. The same single-particle potential V, because of its presence in H', also determines the goodness (i.e., convergence) of the perturbation series.

The BG formulation results in the well-known linked-cluster expansion expression for the energy of the total system[4]:

$$E=E_0+\sum_n^{\infty}{}^{L}\langle\Phi_0|H'[(E-H_0)^{-1}H']^n|\Phi_0\rangle\,. \tag{3}$$

Here we sum over only the "linked" terms while the "unlinked" terms containing the spurious divergences simply do not appear.

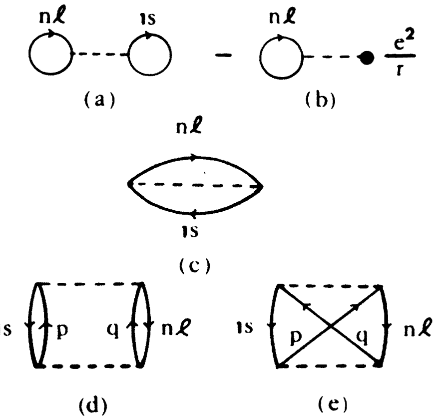

FIG. 1. Leading first- and second-order terms.

III. APPLICATION TO HELIUM $(1s,nl)$ RYDBERG STATES

We must first choose the single-particle potential V for the present calculation. The physics of the helium $(1s,nl)$ atomic Rydberg states $(l\geqslant 2)$ suggests quite naturally the following choice:

$$\begin{aligned} &V=0,\quad \epsilon_n=-4/n^2 \quad \text{for } l=0,1 \text{ orbitals}\,,\\ &V=e^2/r,\quad \epsilon_n=-1/n^2 \quad \text{for } l=2,3,\ldots \text{ orbitals}\,. \end{aligned} \tag{4}$$

The above choice will lead to hydrogenic φ_n's with $Z_{\text{eff}}=2$ for s and p basis orbitals and hydrogenic ϕ_n's with $Z_{\text{eff}}=1$ for d, f, g basis orbitals. Note that two different sets of *radial* orbitals are used here. However, orthogonality of the total basis states is still strictly maintained through the angular momentum eigenfunctions.

The zeroth-order energy E_0 is now simply

$$E_0(1s,nl)=-(4+1/n^2)\ \text{Ry}\,. \tag{5}$$

The level shifts Δ from this Bohr level is simply the sum of all higher-order energy terms.

$$\Delta=E_1+E_2+\ldots\,. \tag{6}$$

We would like to stress the advantage of the present choice of V. Since the "unperturbed" $(1s,nl)$ levels are "degenerate" in l, we may effectively study the relations of level shifts for different l levels from a common starting point. This important advantage will be lost should one choose instead Hartree-Fock-type basis states, as one would normally do in hopes of gaining better convergence.

One may now proceed to draw all the topologically distinct diagrams that represent the contributing terms in the perturbation expansion. The present two-electron system, of course, makes this enumeration particularly simple. The important diagrams up to second-order terms are given in Fig. 1; other second-order diagrams which contribute less numerically are given in Fig. 2. Still higher-order diagrams are illustrated in Fig. 3. The physical interpretations of the important lower-order diagrams can be given as follows.

Screening effect. The sum of diagrams 1(a) and 1(b) (with a minus sign) gives the contribution to the level shift owing to the incomplete screening of the inner $1s$ electron. That is, since the "unperturbed" nl hydrogenic orbital assumes complete screening by the $1s$ electron, these two diagrams correct for this assumption by taking into account the small penetration of the nl electron *inside* the $1s$ core orbital electron.

First-order exchange term. Figure 1(c) represents the contribution of the first-order exchange between the two electrons. This exchange contribution will have opposite sign for spin-singlet and spin-triplet cases.

Polarization and distortion effects. Diagram 1(d) corresponds to the dominant second-order direct terms of the perturbation expansion. Physically this diagram describes the mutual polarization and distortion between the atomic electrons because of their mutual Coulomb repulsions. As diagram 1(d) indicates, the $1s$ electron and nl electron, through their Coulomb interaction, "excite" into intermediate virtual states p and q, respectively, before "deexciting" again back to $1s$ and nl orbitals. Thus, this diagram gives the leading contribution of the effects of the inter-electronic correlations. By multipole expansion

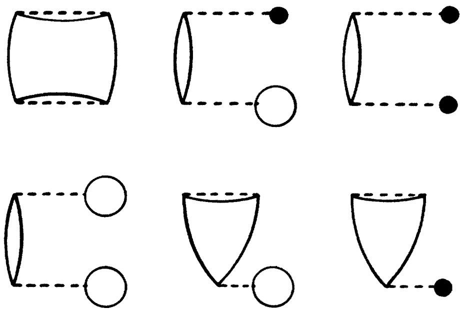

FIG. 2. Other types of second-order terms.

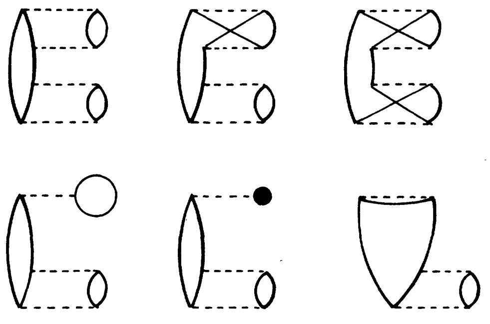

FIG. 3. Some third- and higher-order terms.

of the Coulomb interaction, we can further separate the polarization effects into contributions from monopole, dipole, quadrupole interactions, etc.

Second-order exchange effects. Diagram 1(e) is the exchange counterpart of diagram 1(d) and represents the additional contribution to the exchange energy when interelectronic correlation and polarization are taken into account. Again the sign of this second-order exchange contribution must be opposite for the spin-singlet and spin-triplet cases.

One can make similar physical interpretations for the diagrams in Figs. 2 and 3. However, since their contributions are far less than those in Fig. 1, we shall not detail them here.

Finally we mention that in order to obtain the *average* level shift values, one only needs to evaluate the direct diagrams—the exchange diagrams cancel formally. On the other hand, to obtain the doublet-splitting values between the spin-singlet and spin-triplet levels, one only needs to evaluate the exchange terms—the direct terms cancel formally. Because of this formal cancellation of terms, numerical accuracy is now possible, even in the evaluation of the small doublet splittings.

IV. RESULTS AND DISCUSSIONS

Based on theoretical formulation described in Secs. II and III, we have evaluated up to and including all second-order terms and obtained results for helium Rydberg $(1s, nl)$ states for $n = 3-11$ and $l = 2-4$ $(D,\ F,\ G)$. These results are presented in a number of tables listed below. In Table I we list the absolute level shifts, the shifts from the Bohr level energies $(4 + 1/n^2)$ Ry. For better comparison with experiment, we present the level-transition energies in Table II and the level (doublet) splittings in Table III. To study the effects of different physical processes, we illustrate, in Table IV, a detailed breakdown of the contributions from their corresponding diagrams.

TABLE I. Level shift from zeroth-order energy (in units of 10^{-6} Ry).

n	${}^1D_2$	${}^3D_2$	${}^1F_3$	${}^3F_3$
3	−126.762	−157.599		
4	−56.263	−76.129	−9.7339	−9.9460
5	−31.029	−41.322	−5.5875	−5.7003
6	−18.345	−24.673	−3.4505	−3.5181
7	−11.704	−15.826	−2.2629	−2.3064
8	−7.912	−10.733	−1.5625	−1.5921
9	−5.589	−7.600	−1.1180	−1.1390
10	−4.090	−5.570	−0.8240	−0.8394
11	−3.081	−4.202	−0.6242	−0.6359

Two sets of experimental results are available for comparison with the present theoretical calculation. The experimental results compiled by Martin[1] are from spectroscopic data. Because of its inherent resolution, these spectroscopic data, while very extensive, tends to be less reliable especially for high-nl states. The recent microwave-optical data of Lamb and co-workers[2] should be extremely accurate. Therefore comparison with their results should be more meaningful in spite of the relative paucity of their data points.

Aside from the good over-all agreement with experiments, term-by-term comparison of our calculation with the WLL data[3] shows a consistent difference of (1.5–2)%. In our evaluation of the contributing second-order diagrams, a differential-equation approach[6] was used instead of the usual matrix-element summation method. This gives improved numerical accuracy and enables us to obtain with confidence, values of three significant numbers. Thus the difference must come from the higher-order terms, illustrated in Fig. 3 but not evaluated in the present calculation. We remark that the evaluation of those diagrams is quite feasible and that therefore agreement with

TABLE II. Singlet-triplet splittings (in MHz).

	${}^1D_2-{}^3D_2$		${}^1F_3-{}^3F_3$		${}^1G_4-{}^3G_4$
n	Theory	Expt. [a]	Theory	Expt. [b]	Theory
4	58.78×10^3	59.20×10^3			
5	33.90×10^3	34.41×10^3	371.1	(369.8) [c]	
6	20.82×10^3	20.81×10^3	222.4	(225.3)	121.0
7	13.56×10^3	14.78×10^3	143.1	146.2	76.19
8	9.282×10^3	10.79×10^3	97.31	(99.8)	51.04
9	6.615×10^3	7.196×10^3	69.09	(71.0)	35.85
10	4.870×10^3	5.687×10^3	50.78	51.3	26.31
11	3.688×10^3	4.498×10^3	38.34	39.5	19.63

[a] Reference 1.

[b] Reference 2.

[c] Experimental values given in parentheses are obtained from Eq. (4) of Ref. 2.

TABLE III. Comparisons between the results of the present calculation and available experimental data for various transitions (in GHz).

	$^1D_2-F$ (ave)			$^3D_2-F$ (ave)			F (ave) $-$ G (ave)	
		Expt.			Expt.			
n	Theory	Martin[a]	WLL[b]	Theory	Martin[a]	WLL[b]	Theory	Expt. (WLL)[b]
4	159.31	162.70	(163.34)[c]	218.08	221.89	···	···	···
5	83.51	83.77	(85.22)	117.38	118.18	···	···	···
6	48.89	49.02	(49.81)	69.71	69.83	···	8.742	···
7	30.99	31.51	31.49	44.55	46.29	···	5.620	5.607
8	20.84	18.89	(21.23)	30.12	29.68	···	3.859	···
9	14.68	15.59	(14.95)	21.29	22.79	21.76	2.739	···
10	10.72	10.90	10.90	15.59	16.60	···	2.01	···
11	8.064	8.20	8.20	11.75	12.70	···	1.518	···

[a] Reference 1.

[b] Reference 2.

[c] Experimental values given in parentheses are obtained from Eq. (4) of Ref. 2.

experiment to third significant number, if so desired, can be achieved within the present formulation.

The detailed breakdown of contributing diagrams, as illustrated in Table IV, enables us to observe some systematics and to assess the relative importance of the various physical effects involved. First, we notice the fact that this relative importance seems to be dependent only as a function of l value but is nearly independent of n values. For example, the screening effect contributes about 7% of the total level shift for D states ($l=2$), indicating still appreciable penetration of the outer electron into the 1s core region. For F states ($l=3$), it is already down to ~0.3%; and for G states ($l=4$), it becomes completely negligible. The dominant contribution to the level shifts is the dipole polarization term, ranging from ~ 89% for $l=2$ states, to ~ 98% for $l=3$ states, to an overwhelming ~ 99.5% for $l=4$ states.

With regard to the doublet level splitting values, the most striking result is the importance of the second-order exchange contributions. Since it is opposite in sign to the first-order exchange contribution but comparable in magnitude, the resultant sum is vastly different from the value of first-order exchange alone, which has been used in essentially all previous calculations.[7,8] With the inclusion of second-order exchange, our net level splitting for $l=2$ states is reduced by a factor of 1.7 from that of first-order exchange alone. For $l=3$ states, this factor is about 2.4; and for $l=4$ states it is an even larger 3.3. It is therefore clear that the effect of the second-order exchange must be properly taken into account if good value for the doublet splitting is to be ob-

TABLE IV. Contributions from various physical effects to the level shifts (in units of 10^{-6} Ry)[a]. The plus and minus signs refer to singlets and triplets, respectively.

	Screening	First-order	Second-order direct (polarization)			Second-order		
(n,l)	effect	exchange	monopole	dipole	quadrupole	exchange	Others[b]	Total
(5, 2)	−2.3161	±8.620	−9.98(−2)	−32.2098	−1.3842	∓3.5913	−0.1644 ±0.1155	−36.1742 ±5.1442
(8, 2)	−0.6412	±2.3679	−2.78(−2)	−8.2389	−0.3679	∓0.991	−4.50(−2) ±3.19(−2)	−9.3208 ±1.4087
(10, 2)	−0.3374	±1.2437	−1.46(−2)	−4.2616	−0.1918	∓0.5212	−2.35(−2) ±1.67(−2)	−4.8290 ±0.7392
(5, 3)	−1.12(−2)	±4.32(−2)	−2.97(−4)	−5.5550	−7.46(−2)	∓2.53(−2)	−1.17(−4) ±8.92(−5)	−5.6413 ±1.81(−2)
(8, 3)	−4.16(−3)	±1.59(−2)	−1.10(−4)	−1.5482	−2.41(−2)	∓9.26(−3)	−4.38(−5) ±3.34(−5)	−1.5767 ±6.67(−3)
(10, 3)	−2.32(−3)	±8.84(−3)	−6.30(−5)	−0.8160	−1.30(−2)	∓5.15(−3)	−2.43(−5) ±1.86(−5)	−0.8314 ±3.71(−3)
(7, 4)	−1.64(−5)	±6.38(−5)	−3.14(−7)	−0.5727	−2.62(−3)	∓4.44(−5)	−3.18(−8) ±2.55(−8)	−0.5754 ±1.94(−5)

[a] Numbers in parentheses indicate the powers of 10 by which the entries are to be multiplied.

[b] Sum of all terms given in Fig. 2.

tained. Here it is interesting to note that the importance of this second-order exchange term has previously been observed in electron-atom scattering problems.[9] The present calculation suggests that it should be equally important for bound-state systems such as the Rydberg states—perhaps not too surprising in view of the close relationship between the Rydberg series and the low-energy scattering problems.

We mention that for $l \geqslant 3$ states, the spin-orbit interaction becomes significant; and the mixing effect resulting from this spin-orbital coupling must be and have been included in our calculation through the use of the formalism given by Araki[7] and Parish and Mires[8] with the exchange integral calculated up to second order.

We also mention that for average level shift values, a polarization-model calculation has been carried out by Deutsch.[10] However, the polarization model implicitly contains adiabatic approximation and further is not amenable to predictions of doublet splittings. These limitations as well as some numerical irregularities contained there prevent us from making a meaningful comparison.

Finally we turn to the systematics in n values. Theoretical arguments[11] suggest that for a given l value the level shifts (hence the transition energies) as well as level splittings should behave as a function of n in the form of $(A/n^3+B/n^5)$ for large n values. This parametrization was used in the analysis of the results of WLL.[2] In fact, the results in parentheses in Tables II and III are obtained in this way.

Our numerical results do confirm this and the parametrization is seen to work extremely well even for very-low n values. Thus for a given n series, once two data points are obtained, the parametrization can be used with confidence in predicting the values of other members in the series.

In conclusion, we are encouraged by the result of this calculation, not only in the quantitative aspect but also in the qualitative understanding of the physical effects involved. The generality of the approach makes it readily applicable to other atomic cases. These are being investigated to further assess the potentialities and the limitations of this approach.

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[1] W. C. Martin, J. Phys. Chem. Ref. Data 2, 257 (1973).

[2] W H. Wing and W. E. Lamb, Jr., Phys. Rev. Lett. 28, 265 (1972); W. H. Wing, K. R. Lea, and W. E. Lamb, Jr., *Atomic Physics*, edited by S. J. Smith and G. K. Walters (Plenum, New York-London, 1973), Vol. 3, p. 119.

[3] Part of the present data were presented in an invited talk (R. T. Poe) at the Third International Conference on Atomic Physics (unpublished); R. T. Poe and T. N. Chang, *Atomic Physics*, edited by S. J. Smith and G. K. Walters (Plenum, New York-London, 1973), Vol. 3, p. 143.

[4] J. Goldstone, Proc. R. Soc. Lond. A239, 267 (1957).

[5] H. P. Kelly, Phys. Rev. 131, 684 (1963); E. S. Chang, R. T. Pu (Poe), and T. P. Das, Phys. Rev. 174, 1 (1968); 174, 16 (1968); T. N. Chang, T. Ishihara, and R. T. Poe, Phys. Rev. Lett. 27, 838 (1971); T. Ishihara and R. T. Poe, Phys. Rev. A 6, 116 (1972).

[6] The differential-equation approach is a two-particle extension of the one-particle method used in A. Dalgarno and J. T. Lewis, Proc. R. Soc. Lond. A233, 70 (1955); C. Schwartz and J. J. Tieman, Ann. Phys. (N.Y.) 6, 178 (1959). See also T. N. Chang and R. T. Poe, J. Comp. Phys. 12, 557 (1973) and T. N. Chang, Ph.D. dissertation (University of California, Riverside, 1972) (unpublished).

[7] G. Araki, Proc. Phys.-Math. Soc. Jap. 19, 128 (1937).

[8] R. M. Parish and R. W. Mires, Phys. Rev. A 4, 2145 (1971).

[9] R. T. Pu (Poe) and E. S. Chang, Phys. Rev. 151, 31 (1966); W. M. Duxler, R. T. Poe, and R. LaBahn, Phys. Rev. A 4, 1935 (1971).

[10] C. Deutsch, Phys. Rev. A 2, 43 (1970); 3, 1516(E) (1971).

[11] B. Edlén, Handb. Phys. 27, 80 (1964); T. N. Chang, J. Phys. B 7 (1974).