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Comments on the hyperfine structure of the $4\,^2D$ state of rubidium

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In a recent paper Lee, Rodgers, Das, and Sternheimer have reported on the evaluation of the fine and hyperfine structure of the $4\,^2D$ state of the rubidium atom by considering the first-order polarization of the electron core. By means of more extensive calculations we have shown that the first-order results can be quite unreliable for such strongly perturbed systems. By including polarization effects to all orders and the most important correlation effects, we have been able to reproduce the experimental results for this state quite well. The good agreement obtained by Lee *et al.* for the spin-dipole parameter is in our opinion largely fortuitous.

In a recent paper, Lee, Rodgers, Das, and Sternheimer[1] have reported on calculations of the fine and hyperfine structure of the $4\,^2D$ state of the rubidium atom. By considering the lowest-order polarization of the electron core, caused by the exchange interaction with the valence electron, they have been able to reproduce the negative sign found experimentally[2] for the spin-orbit and spin-dipole parameters. We have for a long time been engaged in similar calculations, and it is our experience that the perturbation expansion usually converges very slowly for the highly perturbed d states of the alkali atoms. Furthermore, the low-order results depend quite critically upon the potential employed. As a consequence, results based on first-order perturbation are quite unreliable. It turns out that the inclusion of higher-order terms can change the results drastically—in some cases even change the sign of the interaction parameter. We wish to illustrate this with the hyperfine structure of the $4\,^2D$ state of rubidium, where extensive calculations have now been performed.[3]

To evaluate the first-order corrections to the zeroth-order (Hartree-Fock) result, Lee *et al.* utilize the technique with inhomogeneous single-particle equations for a long time used by Sternheimer in his calculations of the quadrupole shieldings.[4] We employ a similar technique in our calculations, and solve in addition inhomogeneous two-particle (pair) equations. By means of (first-order) one- and two-particle functions, it is possible to evaluate also the second-order corrections to the Hartree-Fock result.[5] In this way, the effect of the correlation (multiple excitations) upon the hyperfine interaction can be estimated, in addition to the polarization (single-particle) effect. This procedure works very well for the alkali s and p states, but fails almost entirely for the d states.

It can be shown that higher-order polarization effects of the random-phase-approximation (RPA) type can be included in the first-order polarization by choosing the potential in the single-particle equations properly.[6] Such a potential can be handled in the same way as an ordinary HF potential. From Table I it can be seen that the first-order results obtained with an HF potential (i.e., the HF potential of the closed-shell Rb^+ ion) and with the RPA potential are considerably different. The spin-dipole results differ by a factor of 2.5. The two values bracket here the experimental value, as well as the first-order value obtained by Lee *et al.* This illustrates the sensitivity of the first-order results to the potential chosen, and may explain why the calculation of Lee *et al.* yields a good result for the spin-orbit parameter, but not for the other ones.

It is quite clear, though, that higher-order effects are in the present case very important—regardless of the choice of potential. In order to go beyond the RPA model, we have developed a procedure for solving also the *coupled* single-particle equations self-consistently, which means that the mixing between different single-particle excitations can be taken into account to an arbitrary order[7] (in the tables denoted "complete polarization"). It is found that this mixing has only a small effect on the orbital and spin-dipole parameters, while for the contact interaction it amounts to almost 40%. Here, the mixing between the excitations $4s\rightarrow s$ and $4p\rightarrow p$ is particularly important.

However, also when the complete polarization is considered, the agreement with experiment is quite poor. The orbital parameter even comes out with the wrong sign. This means that the correlation is essentially as important as the polarization. When the lowest-order correlation is included, it can be seen that the orbital parameter turns positive again. But this is the case also for the spin-dipole parameter, which is now in serious disagreement with the experimental value. This is a good illustration of the slow convergence

TABLE I. Calculated hyperfine interaction of the 4 ^2D state of Rb using Hartree-Fock basis orbitals.

	Hyperfine parameters (a.u.) [a]				Hyperfine constants for ^{87}Rb (MHz)	
	Orbital	Spin-dipole	Contact	Quadrupole	$A(^2D_{3/2})$	$A(^2D_{5/2})$
Hartree-Fock	+0.041	+0.041	0	+0.041	+11.6	+5.0
First-order polarization HF	+0.011	−0.024	−0.202	+0.115	+7.7	−5.0
First-order polarization RPA	−0.006	−0.064	−0.278	+0.134	+4.0	−9.3
Complete polarization	−0.009	−0.077	−0.447	+0.129	+8.4	−15.4
Complete polar. + lowest-order corr.	+0.052	+0.011	−0.376	+0.161	+24.8	−6.1
Lee *et al.* (Ref. 1)		−0.054	−0.313			
Experimental						
Ref. 2(a)	+0.030(3)	−0.053(12)	−0.637(15)	+0.12(10)	+25.1(9)	−16.9(6)
Ref. 2(b)	+0.029(3)	−0.047(12)	−0.625(15)	+0.12(8)		

[a] The values are given in units of a_0^{-3}, where a_0 is the Bohr radius ($a_0^{-3} = 6.7487 \times 10^{24}$ cm^{-3}).

and the unreliability, mentioned earlier, of the low-order perturbation expansion for this kind of system. It is evident that it is necessary to look into the correlation in more detail in order to be able to reach even qualitative agreement with experiments in this case.

In analyzing the correlation effect, we have found that the dominating part is of "self-energy" type, i.e., insertions of multiple excitations into a single orbital line of the diagrams. Most of these effects can be included in an extended single-particle model, and one finds that this leads to approximate Brueckner or "natural" orbitals.[3] By means of our one- and two-particle equations we have evaluated this effect in the lowest order, and it turns out that this has a drastic effect upon the orbital for the valence electron. The reason is that this orbital is very sensitive to the potential due to the high angular momentum. The natural orbital is more contracted than the HF one, due to the attraction of the correlation hole ("Coulomb hole") that the valence electron creates in the core. This effect is in the present case so large that the zeroth-order value is increased by a factor of 2 in going from the HF to the first-order natural orbitals. By means of the new orbitals we have performed the same type of calculations as discussed before (excluding, of course, the correlation that is already included in the orbitals). The results are shown in Table II.

It is now interesting to compare the results in

TABLE II. Calculated hyperfine interaction of the 4 ^2D state of Rb using natural-orbital basis.

	Hyperfine parameters (a.u.)				Hyperfine constants for ^{87}Rb (MHz)	
	Orbital	Spin-dipole	Contact	Quadrupole	$A(^2D_{3/2})$	$A(^2D_{5/2})$
Natural orbitals	+0.083	+0.083	0	+0.083	+23.2	+9.9
First-order polarization HF	+0.025	−0.043	−0.407	+0.185	+16.4	−9.9
First-order polarization RPA	+0.006	−0.090	−0.494	+0.185	+12.4	−14.6
Complete polarization	−0.001	−0.113	−0.783	+0.173	+19.3	−25.2
Complete polar. + lowest-order corr.	+0.041	−0.024	−0.623	+0.174	+28.6	−15.6
Experimental						
Ref. 2(a)	+0.030(2)	−0.053(12)	−0.637(15)	+0.12(10)	+25.1(9)	−16.9(6)
Ref. 2(b)	+0.029(3)	−0.047(12)	−0.625(15)	+0.12(8)		

the two tables. It is found that not only the zeroth-order value but also the polarization is considerably increased, when the HF orbitals are replaced by natural ones. This is evidently a consequence of the deeper penetration of the latter. The lowest-order correlation is essentially as large with natural orbitals as with HF ones—in spite of the fact that important correlation effects are hidden in the natural orbitals. The reason is that a low-order expansion using natural orbitals also contains important effects, which using HF orbitals would appear first in higher orders. As a consequence, a natural-orbital basis is expected to lead to faster convergence than an HF one.

The final results obtained with the natural-orbital basis including complete polarization and lowest-order correlation, are satisfactory, and they constitute a definite improvement over the corresponding results with the HF basis. The A factors now agree with experiments within 15%. The largest discrepancy appears still for the spin-dipole parameter, which is of the correct sign, but a factor of 2 too small. Considering the magnitude of the lowest-order correlation, however, this discrepancy is not surprising. In order to improve the results further, it is necessary to include also higher-order correlations with the natural-orbital basis. This has recently been done by iterating also the (coupled) two-particle equations towards self-consistency, which makes it possible to include essentially all pair correlation. The new results, which agree even better with the experiments than those given here, will be described in a forthcoming publication.

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[1] T. Lee, J. E. Rodgers, T. P. Das, and R. M. Sternheimer, Phys. Rev. A 14, 51 (1976).

[2] (a) K. H. Liao, L. K. Lam, R. Gupta, and W. Happer, Phys. Rev. Lett. 32, 1340 (1974); (b) R. Gupta, reported at the Atomic Spectroscopy Symposium, National Bureau of Standards, Gaithersburg, Md., 1975 (unpublished).

[3] I. Lindgren, J. Lindgren, and A-M. Mårtensson, Z. Phys. A 279, 113 (1976). Preliminary results of these calculations were reported in *Proceedings of the Fourth International Conference on Atomic Physics, Heidelberg*, 1974, edited by G. zu Putlitz (Plenum, New York, 1975), p. 747.

[4] See, for instance, R. M. Sternheimer, and R. F. Peierls, Phys. Rev. A 3, 837 (1971).

[5] S. Garpman, I. Lindgren, J. Lindgren, and J. Morrison, Phys. Rev. A 11, 758 (1975).

[6] See, for instance, T. N. Chang and U. Fano, Phys. Rev. A 13, 263 (1976).

[7] S. Garpman, I. Lindgren, J. Lindgren, and J. Morrison, Z. Phys. A 276, 167 (1976).