

be carried out for the ground state and excited states. Energy differences between the potential curves could then be obtained. The rapid convergence of the perturbation expansion confirms the acceptability in this case of using carbon rather than nitrogen, the united atom, as a starting point.

We plan to use these methods to calculate many additional properties of CH.

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## Locality of the Effect of the Pauli Principle in Atoms

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It is shown that the conventional application of the Pauli principle to the qualitative estimation of the relative distributions of electrons with parallel and antiparallel spins is wrong. The Pauli principle induces a local reduction of the probability of finding electrons with parallel spins close together. However, for neutral atoms at least, such electrons have a considerably higher probability of being found at moderate separations and an accompanying reduced probability of being found at higher separations, relative to electrons with antiparallel spins.

The Pauli principle is usually invoked to argue that in atoms and molecules electrons with parallel spins tend to stay essentially further away than electrons with antiparallel spins. This argument should lead to expectation values of  $1/r_{12}$  being lower and of  $r_{12}$  and  $r_{12}^2$  being higher for the higher multiplicity terms. The interpretation of Hund's rule in terms of the different contributions to the total energy has recently been attempted.<sup>1-4</sup> It has been noticed that, contrary to the customary assumption, the interelectronic repulsion in the higher multiplicity terms is higher than that in the lower multiplicity terms.<sup>1,2</sup> This has been shown to be generally valid for light neutral atoms<sup>4</sup>; for sufficiently highly charged isoelectronic ions the conventionally expected ordering of interelectronic repulsions is generally observed. It has been argued<sup>3</sup> that higher  $\langle 1/r_{12} \rangle$  for the higher multiplicity terms does not exclude the possibility of

$\langle r_{12} \rangle$  being higher for them, and that it is this latter value which measures the average interelectronic distance. Very recently, accurate calculations for the  $1^3P$  terms of the He isoelectronic sequence have become available.<sup>5</sup> They indicate just the trends discussed in Ref. 4. In particular, the values of  $({}^3C - {}^1C)/({}^3L - {}^1L)$ , where  $C$  denotes the interelectronic repulsion and  $L$  the nuclear attraction, are observed to increase from a negative value for the neutral He atom to positive values for the higher members of the isoelectronic sequence. The asymptotic behavior expected on the basis of a perturbation-theoretic argument,<sup>4</sup> namely,  $\Delta C/\Delta L = 1 - \alpha/Z$ ,  $\alpha$  being a constant, is confirmed by these values, presented in Fig. 1. A further check of the results presented in Ref. 5 reveals the hitherto entirely unexpected ordering of  $\langle r_{12} \rangle$  and  $\langle r_{12}^2 \rangle$ . Whereas  $\langle 1/r_{12} \rangle$  becomes lower for the triplet at  $Z=4$ ,  $\langle r_{12} \rangle$  persists in being

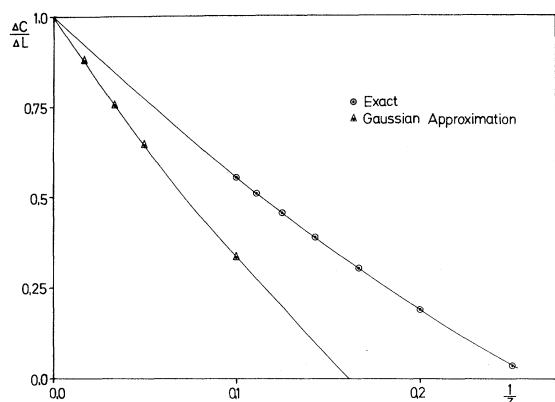


FIG. 1.  $\Delta C/\Delta L$  vs  $1/Z$  for the He  $1,^3P$  isoelectronic sequence.

smaller for the triplet up to  $Z=7$ .  $\langle r_{12}^2 \rangle$  is smaller for the triplet for all the cases considered. These facts indicate the failure of the qualitative predictions concerning the distribution of electrons based on the Pauli principle.

In order to understand these exceedingly disturbing results the  $1,^3P$  terms of the He isoelectronic sequence have been studied in the independent-particle model with  $\phi_{1s} = e^{-\alpha r^2}$  and  $\phi_{2p} = x e^{-\beta r^2}$ .  $\alpha$  and  $\beta$  are variationally determined for each term separately. Some results are presented in Table I, and the ratios  $\Delta C/\Delta L$  are plotted in Fig. 1. The essentially very similar qualitative behavior of the approximate and exact results, which on the basis of Ref. 4 is to be generally expected, indicates that qualitative conclusions based on the approximate model should be of rather general validity. The pair distribution function  $f(r'_{12}) = \langle \Psi | \delta(r_{12} - r'_{12}) | \Psi \rangle$ , which measures the probability of finding the two electrons separated by  $r'_{12}$ , irrespective of all other coordinates, has been eval-

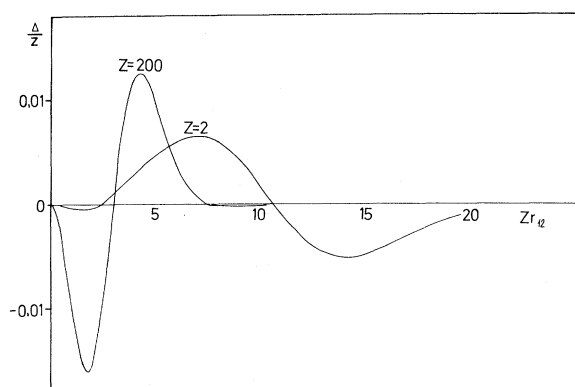


FIG. 2. Difference between the  $^3P$  and  $^1P$  pair distribution functions.

uated for the  $^1P$  and  $^3P$  terms of the He isoelectronic sequence. One gets  $^3f = D - E$  and  $^1f = D + E$ , where

$$D(r) = C \exp\left(\frac{-2\alpha\beta}{\alpha+\beta} r^2\right) r^2 \left[1 + \frac{4\alpha^2}{3(\alpha+\beta)} r^2\right],$$

$$E(r) = C \exp\left(\frac{-(\alpha+\beta)}{r} r^2\right) r^2 \left[1 - \frac{\alpha+\beta}{3} r^2\right],$$

and

$$C = \frac{32\beta}{\sqrt{\pi}(\alpha+\beta)} \left(\frac{\alpha\beta}{2(\alpha+\beta)}\right)^{3/2}.$$

The low- $r$  asymptotic behavior is easily shown to be  $^3f \sim r^4$  and  $^1f \sim r^2$ , which is a manifestation of the Pauli principle. At high  $r$ ,  $E(r)$  vanishes much more rapidly than  $D(r)$  so that the main difference between  $^3f$  and  $^1f$  is due to the difference between  $^3D(r)$  and  $^1D(r)$  originating from the difference between the variational parameters  $\alpha$  and  $\beta$  for the corresponding wave functions. The higher nuclear attraction in the triplet is due to contraction of the  $2p$  orbital which is manifested by the fact that  $^3\beta > ^1\beta$  whereas  $^3\alpha \approx ^1\alpha$ . The large- $r$  asymptotic dependence of  $D$  on the parameters is such that  $^3D < ^1D$  so that  $^3f < ^1f$ . It is, therefore, seen that both at low  $r$  and at high  $r$  the distribution function is higher for the singlet. Due to the fact that each of the distribution functions is normalized such that  $\int_0^\infty f(r) dr = 1$ ,  $^3f$  should be higher than  $^1f$  at the intermediate range of interelectronic separations. If the same parameters  $\alpha$  and  $\beta$  are assumed for both the  $^1P$  and  $^3P$  states then  $^3D = ^1D$  and  $^3E = ^1E$  so that  $^3f - ^1f = -2E$ .  $E(r)$  is positive for  $r < [3/(\alpha+\beta)]^{1/2}$  and negative for higher  $r$ . The distribution function for the triplet is therefore lower at low  $r$  and higher at high  $r$  than that for the singlet. This behavior is the one intuitively referred to on the basis of the Pauli principle. The restriction to equal one-electron orbitals for the singlet and triplet has already been shown to result in the false "normal" ordering  $[^3\langle 1/r_{12} \rangle] < [^1\langle 1/r_{12} \rangle]$ .<sup>1,2</sup>

The computed difference  $\Delta(r_{12}) = ^3f(r_{12}) - ^1f(r_{12})$  is presented in Fig. 2. For the neutral atom the results indicate a higher probability of finding the electrons at intermediate separations when they are in the triplet. The probability of the electrons

TABLE I. Gaussian approximation for the He  $1,^3P$  isoelectronic sequence.

|         |       | $\alpha$ | $\beta$ | $E$      |
|---------|-------|----------|---------|----------|
| $Z=2$   | $^3P$ | 1.1297   | 0.0468  | -1.81162 |
|         | $^1P$ | 1.1330   | 0.0444  | -1.81034 |
| $Z=200$ | $^3P$ | 11314    | 1796    | -21460.1 |
|         | $^1P$ | 11320    | 1791    | -21457.4 |

being found highly separated is higher for the singlet. The Pauli principle is manifested by the behavior of  $\Delta(r_{12})$  for small  $r_{12}$ . It is noted that in this range the triplet distribution is lower. The Pauli principle is satisfied, but the extrapolation of the local behavior predicted by it at  $r_{12} \approx 0$  to higher values of the interelectronic separation is totally misleading. For the isoelectronic ion with  $Z=200$ , the behavior of  $\Delta(r_{12})$  is just the one conventionally expected, namely, a relatively higher probability of finding the electrons close together

in the singlet and an accompanying higher probability of finding them well separated in the triplet. This behavior explains the "paradoxical" values of  $\langle 1/r_{12} \rangle$ ,  $\langle r_{12} \rangle$ , and  $\langle r_{12}^2 \rangle$ . It is obvious that the qualitative features of the pair distributions are of general validity and, therefore, that the qualitative application of the Pauli principle for any but well-localized effects in terms of the interelectronic separation is completely unjustified.

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## Effect of a Diffuse Nuclear Charge Distribution on the Hyperfine-Structure Interaction\*

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A diffuse nuclear charge distribution, with approximately the trapezoidal Hofstadter shape, is used to calculate the effect of the distributed nuclear charge on the magnetic-dipole hyperfine-structure (hfs) interaction between the nucleus and the atomic electron. For a surface or a uniform charge distribution model this effect is known as the Breit-Rosenthal-Crawford-Schawlow correction to the point-charge interaction. The hfs interactions calculated with the diffuse and with the uniform charge distributions differ by over 4% for medium to heavy nuclei. The results, combined with our previously calculated values for the Bohr-Weisskopf correction (the effect on the hfs due to the nonpunctual distribution of nuclear magnetization), allow a more realistic determination of the total hfs anomalies, caused by the extended nuclear electric and magnetic structures, and therefore also of  $|\psi(0)|^2$ , the probability of the electron wave function at the origin.

### I. INTRODUCTION

The electric and magnetic interactions of atomic electrons in penetrating orbits ( $s$  and  $p_{1/2}$ ) with the nucleus are sensitive to the extension of nuclear electric and magnetic structure. These electron-nuclear interactions can therefore serve in turn to probe details of the nuclear structure.<sup>1</sup> Because of the great sensitivity of optical techniques, experiments are possible with nanogram or even picogram quantities of isotopes and therefore allow systematic studies over an extensive range of mass numbers. (In mercury, these cover now 21 mass numbers, and include several nuclear isomers.) Recently, we have reported such systematic results for the magnetic interactions<sup>2</sup> and earlier for the electric case.<sup>3</sup> We have extended these now to isotopes with a half-life of a few hours by a novel

technique combining optical pumping and Zeeman scanning with optical detection.<sup>4</sup> Otten and co-workers have reported such optical results, but with the use of  $\beta$ -decay asymmetry detection, for isotopes in a quantity as small as  $2 \times 10^7$  atoms (done on-line with the accelerator) and a half-life as short as 8.8 sec.<sup>5</sup> Though such nuclear-structure studies can of course be done advantageously with  $\mu$ -mesic atoms,<sup>6</sup> they are limited at present to work with stable isotopes since the experiments require some ten orders of magnitude more isotopic material.

Theoretical exploitations of such systematic studies have been initiated for the electric case, based on the isotope shifts in the monopole part ( $k=0$ ) electron-nuclear interaction.<sup>7</sup> For the magnetic case, Bohr and Weisskopf<sup>8</sup> have calculated the effect on the magnetic-dipole ( $k=1$ ) hyperfine-