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ABSTRACT

An examination is made of the hyperfine structures of those levels comprising the ground configurations $1s^2 2s^2 2p^N$ of the neutral atoms B, C, N, O, and F. Perturbation theory is used to study the effects of configuration interaction, thereby exhibiting the dependence of these effects on the quantum numbers defining the levels. Relativistic effects are considered. The importance of including the $s \rightarrow d$ excitations as well as those of the type $p \rightarrow p'$ is stressed.

1. INTRODUCTION

The five neutral atoms B, C, N, O, and F possess the ground configurations $1s^2 2s^2 2p^N$, where N runs from 1 to 5. Accurate hyperfine-structure (hfs) measurements on low-lying levels have been made for a number of isotopes.¹⁻⁶ It can easily be seen that a theory based simply on an open shell of 2p electrons is inadequate, since such a theory predicts null values for the constant A in the effective Hamiltonian $A \mathbf{I} \cdot \mathbf{J}$ for the $^4S_{3/2}$ level of p^3 , in contradiction to experiment.³ The origin of the finite value for $A(^4S_{3/2})$ is mainly core polarization.⁷ Configurations involving excitations of the type $s \rightarrow s'$ (such as $1s^2 2s 2p^N 3s$) can be coupled to the ground configuration by the exchange interactions between the s electrons and the p shell, thereby leading to an unpaired s -electron spin-density at the nucleus.

The recent work of Harvey⁶ demonstrates in a striking way that other types of configuration interaction play a role. To fit his experimental data on O^{17} and F^{19} , he was forced to replace the radial parameter $\langle r^{-3} \rangle$ characteristic of a 2p electron by two parameters, $\langle r_l^{-3} \rangle$ and $\langle r_s^{-3} \rangle$ associated with the orbital and spin parts respectively of the hfs Hamiltonian. An elaborate Hartree-Fock (HF) calculation, based on the assumption that this effect is due to excitations of the type $p \rightarrow p'$, leads to values of $\langle r_s^{-3} \rangle / \langle r_l^{-3} \rangle - 1$ that are too small for both atoms by factors of between 2 to 3.⁸ On the other hand, the observed core polarization is satisfactorily accounted for.

It seems useful to review the various effects of configuration interaction on hyperfine structures throughout the entire 2p shell. Perturbation theory will be used. It has the advantage over any HF method in that it throws into sharp relief the dependences of these effects on S and L (the quantum numbers of the total spin and total orbital angular momenta) as well as on N .

2. PERTURBATION MECHANISMS

Since the hfs operator is the sum of single-electron operators, all first-order corrections to hyperfine structures due to configuration interaction involve the excitations of one electron at a time. Only four types of excitation are allowed: $s \rightarrow s'$, $s \rightarrow d$, $p \rightarrow p'$, and $p \rightarrow f$. Each is now considered in turn.

(a) $s \rightarrow s'$. As already mentioned, this corresponds to core polarization. Its effect can be reproduced by the operator⁹

$$(2\beta_N \mu_N / I)(8\pi/3) \Gamma \underline{S} \cdot \underline{I} a_0^{-3}$$

acting solely within the p^N shell, where

$$\Gamma = 2 \sum_{\tau} a_0^{-3} R^3(2p, ns, s', 2p) \psi_{ns}(0) \psi_{s'}(0) / 3W(ns, s')$$

In these expressions, β is the Bohr magneton, β_N the nuclear magneton, μ_N the nuclear moment (in nuclear magnetons), a_0 the Bohr radius, $R^3(2p, ns, s', 2p)$ a Slater integral, $\psi_{\tau}(0)$ the amplitude of the eigenfunction τ at the nucleus, and $W(ns, s')$ the (positive) energy of excitation. The sum runs over $n = 1$ and 2 , and over all excited eigenfunctions s' (including those in the continuum).

Since $\underline{S} = \underline{L} + 2\underline{S} - \underline{J} = (g-1)\underline{J}$, core polarization gives a contribution ΔA to the hyperfine constant A of a level, where

$$\Delta A = (g-1)(2\beta_N \mu_N / I)(8\pi/3) \Gamma a_0^{-3}$$

(b) $s \rightarrow d$. Owing to the selection rule $\Delta l = 2$ in the orbital space, this type of excitation affects only two hfs operators: the spin part

$$-(2\beta\beta_N\mu_N/I)(10)^{1/2} \sum_i (\underline{s} \cdot \underline{C}^{(2)})_i^{(1)} \cdot \underline{I}/r_i^3$$

of the magnetic hfs interaction, and the electric quadrupole interaction.

(The symbol $\underline{C}^{(2)}$ stands for the usual second-rank tensor.¹⁰) A detailed calculation¹¹ reveals that we can reproduce the effect of the excitations $s \rightarrow d$ by replacing the ordinary diagonal integral $\langle r^{-3} \rangle$ for the spin part of the 2p-electron hfs by $(1+\xi_s)\langle r^{-3} \rangle$, where

$$\xi_s = 2 \sum (ns | r^{-3} | d) R^1(2p \ ns, d \ 2p) / 3(2p | r^{-3} | 2p) W(ns, d) ,$$

in which the sum runs over $n = 1$ and 2 , and all excited configurations d . Since this type of excitation does not affect the orbital part of the hfs operator, we may write $\xi_l = 0$.

In a similar way, the effect of these excitations on the quadrupole part of the hfs operator can be reproduced by replacing $\langle r^{-3} \rangle$ by $(1+\xi_q)\langle r^{-3} \rangle$, where

$$\xi_q = 2 \sum (ns | r^{-3} | d) [5 R^1(2p \ ns, d \ 2p) - 6 R^2(2p \ ns, 2p \ d)] / 15(2p | r^{-3} | 2p) W(ns, d).$$

(c) $p \rightarrow p'$. This type of excitation is slightly more difficult to treat than those so far considered, since the open shell that produces the hfs is itself disturbed. The simplest approach is to consider all possible determinantal product states of $2p^{N-1}p'$ that can couple to a particular state of $2p^N$. The effect of the interaction can be reproduced by multiplying $\langle r^{-3} \rangle$ for a $2p$ electron by a factor $(1+\eta_\ell)$, $(1+\eta_s)$, or $(1+\eta_q)$, depending on the part of the hfs operator under study. Unlike ξ_ℓ , ξ_s , and ξ_q , the quantities η vary from multiplet to multiplet. They are conveniently expressed in terms of the parameter x , given by the equation

$$x = \sum_p (2p|r^{-3}|p') R^2(2p\ 2p, 2p\ p') / 25(2p|r^{-3}|2p) W(2p, p').$$

A complete listing for the configurations p^N is set out in Table 1.

If we wish, we can reproduce Table 1 by an effective operator acting solely within the $2p$ shell. Suppose we denote a particular hfs operator by $\mathbb{T}^{(\kappa\kappa)}$ [either $\sum \ell / r^3$, $\sum (\underline{s} \underline{c}^{(2)}) / r^3$, or $\sum \underline{c}^{(2)} / r^3$ according as $(\kappa\kappa) = (01)$, $(i2)$, or (02)]. We have merely to replace $\mathbb{T}^{(\kappa\kappa)}$ by

$$\mathbb{T}^{(\kappa\kappa)} + \mathbb{X}^{(\kappa\kappa)},$$

where $\mathbb{X}^{(\kappa\kappa)}$, like $\mathbb{T}^{(\kappa\kappa)}$, acts within the $2p$ shell and is defined in terms of the unit double tensors $\underline{u}^{(\kappa\kappa)}$ by the equation

$$\begin{aligned} \mathbb{X}^{(\kappa\kappa)} = & -30 \sqrt{2x} (2p || \mathbb{T}^{(\kappa\kappa)} || 2p) (2k+1)^{-1/2} \\ & \times \sum_{i \neq j} \sum_{k'} (2k'+1) [(-1)^k + (-1)^{k'}] W(k'k11; 21) \{ \underline{u}_i^{(\kappa\kappa')} \underline{u}_j^{(02)} \}^{(\kappa\kappa)}. \end{aligned}$$

This formula is useful for constructing a check on Table 1. For a given κ and k , we find that

$$\eta(p^N_{SL}) + \eta(p^{6-N}_{SL}) = x[20+60(-1)^k W(1111; k^2) - 24\delta(\kappa, 0) \delta(k, 2)] .$$

It can be seen that for a half-filled shell, η is independent of S and L . This gives an explanation for the rows of Table 1 labelled $2p^3 \ ^2D$ and $2p^3 \ ^2P$ being the same.

(d) $p \rightarrow f$. For atoms as light as those considered here, one has to go far into the continuum before an appreciable overlap between an f eigenfunction and a $2p$ eigenfunction occurs. Compared to excitations of the type $p \rightarrow p'$, those in which f -electron states are involved must lead to effects that are extremely small. They are therefore neglected.

3. RELATIVISTIC EFFECTS

Before making a direct comparison between theory and experiment, it is convenient to briefly consider the corrections due to relativity. As pointed out by Sandars and Beck,¹² the effect of relativity on the magnetic part of the hfs interaction can be reproduced by including the appropriate factors $(1+\lambda_l)$ or $(1+\lambda_s)$ and augmenting Γ by $\Delta\Gamma$. From an observational standpoint, relativistic effects are thus inextricably blended with the effects of configuration interaction. On the basis of Casimir's theory,¹³ we find, to first order in $Z^2\alpha^2$,

$$\lambda_\ell = 83Z^2\alpha^2/80 ,$$

$$\lambda_s = 5441Z^2\alpha^2/2160 ,$$

$$\Delta\Gamma = -119 Z^2\alpha^2 a_0^3 \langle r^{-3} \rangle / 720\pi .$$

The quadrupole part of the hfs is slightly more complicated to treat, since a new tensor having the form $\mathbb{T}^{(11)}$ is required. This will not be considered further because relativistic effects are extremely small for atoms with nuclear charge Z less than 10. This is shown in detail in the next section.

4. COMPARISON WITH EXPERIMENT

From the preceding analysis, we see that the hfs constant A for a level of $1s^2 2s^2 2p^N$ depends on the three parameters Γ , $\langle r_s^{-3} \rangle$, and $\langle r_\ell^{-3} \rangle$. The quadrupole constant B involves a fourth quantity, $\langle r_q^{-3} \rangle$. Each multiplet of the $2p$ shell is characterized by a set of these parameters. By detailed measurements on the levels comprising the multiplets 3P of O^{17} and 2F of F^{19} , Harvey⁶ was able to find Γ , $\langle r_s^{-3} \rangle$ and $\langle r_\ell^{-3} \rangle$ for both multiplets. It turns out that $\langle r_s^{-3} \rangle / \langle r_\ell^{-3} \rangle = 1.13$, $\Gamma = 0.0569$ for 3P of oxygen; the corresponding quantities for fluorine are 1.11 and 0.0717.

Collecting the results of Secs. 2 and 3, we obtain

$$\frac{\langle r_s^{-3} \rangle}{\langle r_\ell^{-3} \rangle} = \frac{(1+\xi_s)(1+\eta_s)(1+\lambda_s)}{(1+\xi_\ell)(1+\eta_\ell)(1+\lambda_\ell)} ,$$

in which, as already pointed out, $\xi_\ell = 0$. Since this ratio depends on N, S, and L, it is remarkable that the two observed ratios (1.13 and 1.11) should be so similar. However, we note from Table 1 that the ratio $(1+\eta_s)/(1+\eta_\ell)$, which alone contains the dependence on S and L, is $(1+12x)$ for 3P of O and $(1+22x)/(1+10x)$ for 2F of F; and in the limit of small x these ratios are identical. It follows that we have only to suppose that the excited orbitals and energies of excitation are roughly the same in the two atoms to understand the constancy of the ratio $\langle r_s^{-3} \rangle / \langle r_\ell^{-3} \rangle$.

The relativistic contribution to $\langle r_s^{-3} \rangle / \langle r_\ell^{-3} \rangle$ is

$$(1+\lambda_s)/(1+\lambda_\ell) = 1 + 40Z^2\alpha^2/27.$$

Setting $\alpha = 1/137$ and $Z=8$ (corresponding to oxygen), we obtain 1.0051. A slightly larger value (1.0069) is obtained if the central field of Herman and Skillman¹⁴ is used.¹⁵ Relativistic effects thus account for only 5 percent or so of the observed deviation of $\langle r_s^{-3} \rangle / \langle r_\ell^{-3} \rangle$ from 1. As for relativistic corrections to core polarization, we find from Sec. 3 that $\Delta\Gamma = -0.0009$ for oxygen. This is only 2 percent of the observed figure.

Since the ground level of N is ${}^4S_{3/2}$, the origin of the observed³ A value must be almost entirely core polarization. We find $\Gamma = 0.0324$. This figure compares fairly well with the value 0.0421 obtained by linearly extrapolating the F and O results.

Insufficient data are available to analyze the ground multiplet 3P of C. Nevertheless, it is worth noting that for 3P_1 ,

$$A = (\beta\beta_{N^+N}/I)[\langle r_\ell^{-3} \rangle - \langle r_s^{-3} \rangle + (8\pi/3)\Gamma a_0^{-3}].$$

This is zero for a pure configuration $1s^2 2s^2 2p^N$. The small observed value² leads to $\Gamma = 0.0045$ if it is assumed that $\langle r_\ell^{-3} \rangle = \langle r_s^{-3} \rangle$. On the basis of the results for N, O, and F, this value for Γ seems too small. However, a modest value of 1.050 for $\langle r_s^{-3} \rangle / \langle r_\ell^{-3} \rangle$ would allow Γ to be increased to 0.015, assuming $\langle r_s^{-3} \rangle = 1.71 a_0^{-3}$ (see Ref. 2). It therefore appears that the carbon results, as they stand at present, can be fitted without difficulty into the general theoretical scheme developed here.

5. EIGENFUNCTIONS

There remains the question of the actual numerical values of Γ , $\langle r_s^{-3} \rangle$, and $\langle r_\ell^{-3} \rangle$. The extensive HF calculations already performed^{7,8} appear to give entirely satisfactory results except for one point: the deviation of $\langle r_s^{-3} \rangle / \langle r_\ell^{-3} \rangle$ from 1. Rather than follow the HF approach, it was felt that it would be more in keeping with the methods described here to attempt to derive ξ_s and x from the infinite sums of Secs. 2(b) and 2(c). An analysis of this kind is of considerable interest in itself, since it leads to a knowledge of the relative importance of different parts of the continuum. Oxygen was chosen as a representative atom.

The radial eigenfunctions R'/r are conveniently found by putting an electron l in the central potential given by Herman and Skillman.¹⁴ Eigenfunctions in the continuum are trivial to generate; it is only necessary to pick a (positive) energy E and integrate out from the origin, starting with $R' \sim r^{\ell+1}$ for small r . At large distances from the nucleus they go over into

$$R' = \rho^{-1/2} \exp[i(Kr+\gamma)].$$

In this expression, γ is a phase angle and $a_0 K = (E/E_0)^{1/2}$, where E_0 is 1 Rydberg. The quantity ρ is a normalizing factor, and can be regarded as the radius of a large spherical box at the centre of which the oxygen atom is placed. The procedure consists in selecting a number of values of E , generating the eigenfunctions, and calculating the various radial integrals that appear in the definitions of ξ_s and x . The sums over the continuum states can be estimated by using the fact that the number of eigenfunctions with a given $(l m_s m_l)$ in the energy interval δE is $\rho \delta E (E/E_0)^{-1/2} / 2\pi a_0$. A WKB analysis shows that contributions to either ξ_s or x from a small energy interval just above and just below the ionizing limit are identical. The passage from the discrete states to those in the continuum is thus not accompanied by the onset of any special effects.

For excitations of the type $p \rightarrow p'$, we find $x = 0.0030$. The contribution of the states in the continuum to this number is roughly twice that of the discrete states. For the 3P states of oxygen, this leads to

$$(1+\eta_s)/(1+\eta_l) = 1.035 .$$

This is in satisfactory agreement with the calculations based on the HF method,⁸ which yield ratios mainly in the region of 1.04 to 1.05, depending on the detailed nature of the approximations made. But it still falls far short of the observed figure of 1.13.

Contributions to ξ_s come from the excitations $1s \rightarrow d$ and $2s \rightarrow d$. It was expected that their effect would be quite small, since they are not apparently discussed in the literature. Indeed, it turns out that the contributions from the discrete d eigenfunctions are quite negligible. But as E is

increased beyond the ionizing limit, the contribution for either $1s \rightarrow d$ or $2s \rightarrow d$ coming from a given energy interval E rises to a maximum before declining, and an appreciable effect is produced. Radial eigenfunctions for d electrons near those parts of the continuum where they play their most important role are drawn out in Fig. 1. The $1s$ and $2s$ eigenfunctions, as well as the p eigenfunctions, are included for comparison. The final result is

$$(1 + \xi_s) = 1.025,$$

the $1s \rightarrow d$ excitations contributing approximately twice as much as those of the type $2s \rightarrow d$. Including the small relativistic contribution, we find finally that for the 3P states of O ,

$$\langle r_s^{-3} \rangle / \langle r_d^{-3} \rangle = 1.065 .$$

This still falls short of the experimental value of 1.13, even though all contributions combine with the same sign. The inadequacy of the assumed central field may be mainly responsible for the discrepancy. Perhaps the central field of O^+ would be more suitable for generating the continuum states, though an approach along these lines would not be consistent with a natural development by perturbation theory. Be this as it may, the present calculation establishes the importance of the $s \rightarrow d$ excitations, and it would be of considerable interest to set up the corresponding calculation within the HF framework.

6. CONCLUSION

The calculations described above indicate that the excitations $s \rightarrow d$ and $p' \rightarrow p'$ are of comparable magnitude. This could be checked by measurements of the hfs constants for excited multiplets of the p^N configurations. The 1D_2 level of O^{17} is particularly attractive for this purpose. The unknown quadrupole correction factor $1+\xi_q$ for 1D_2 is the same as for 3P_1 or 3P_2 , and can be eliminated by taking ratios of the B constants. Table 1 indicates that it should be possible to extract a value of x by this procedure. An analysis of $A({}^1D_2)$, taken with Harvey's results for the multiplet 3P , should yield a second value of x , and a comparison of these two figures would be most interesting.

A start on the excited multiplets has recently been made by Evenson and Radford,¹⁶ who have reported preliminary measurements on the hfs of the levels ${}^2D_{3/2}$ and ${}^2D_{5/2}$ of N^{14} . A full analysis should shed some light on the effect of configuration interaction, though the absence of information on $\langle r_s^{-3} \rangle$ and $\langle r_l^{-3} \rangle$ from the ground level ${}^4S_{3/2}$ may make it a delicate matter to draw firm conclusions about the relative importance of the various types of excitation.

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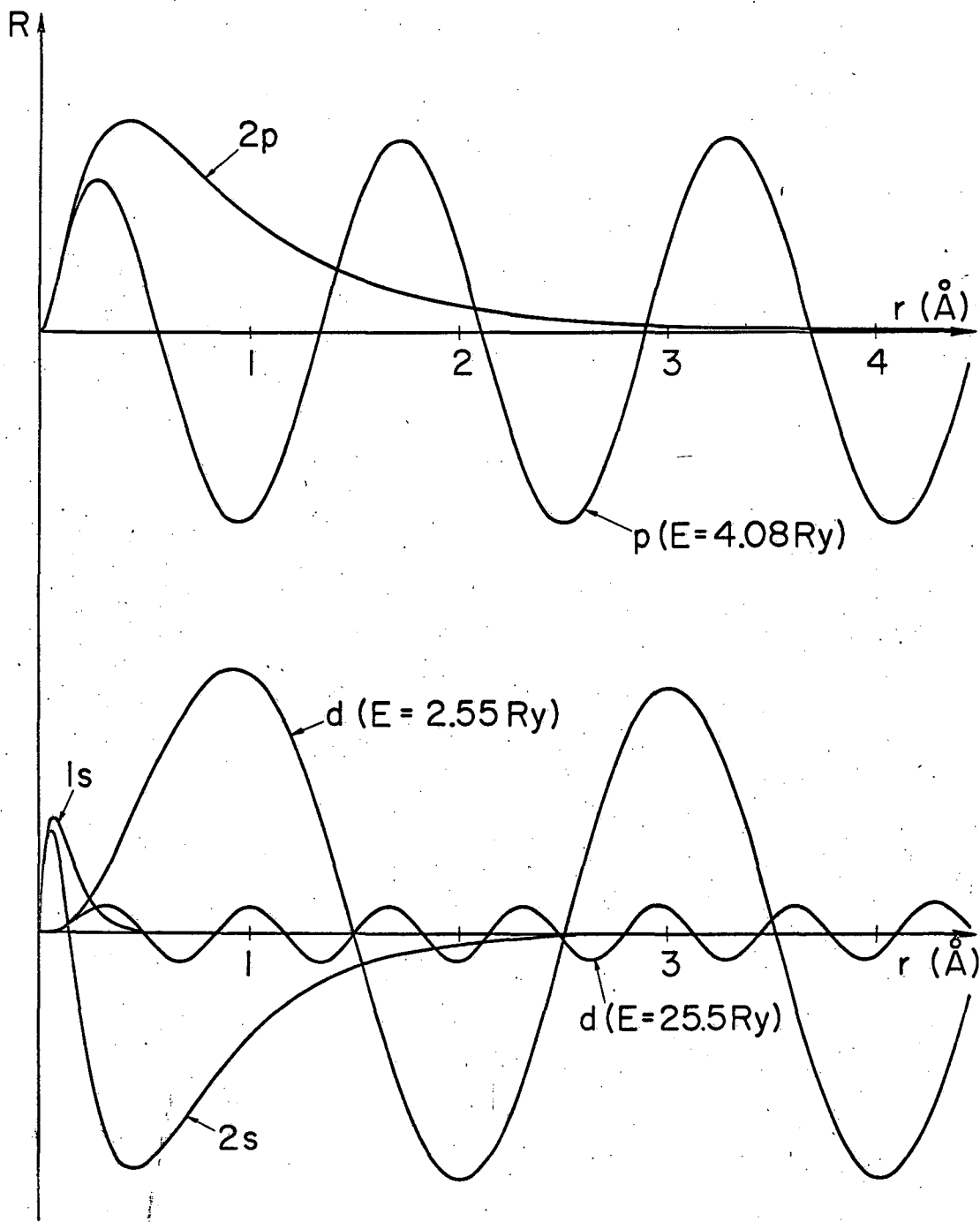
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caption to Figure

Fig. 1. Unnormalized eigenfunctions for the neutral oxygen atom. All eigenfunctions with a given l tend to the same form as $r \rightarrow 0$. The continuum d eigenfunctions are drawn out near energies where $1s \rightarrow d$ and $2s \rightarrow d$ excitations make their most important contributions.

Table 1. Correction factors $(1+\eta)$ to allow for excitations of the type $p \rightarrow p'$.

Configuration	Level	$(1+\eta_l)$	$(1+\eta_s)$	$(1+\eta_q)$
$2p$	2_P	1	1	1
$2p^2$	3_P	$(1+10x)$	$(1+10x)$	$(1+10x)$
	1_D	$(1-2x)$	-	$(1-2x)$
	1_S	-	-	-
$2p^3$	4_S	-	-	-
	2_D	$(1+5x)$	$(1+11x)$	∞
	2_P	$(1+5x)$	$(1+11x)$	∞
$2p^4$	3_P	1	$(1+12x)$	$(1-12x)$
	1_D	$(1+12x)$	-	1
	1_S	-	-	-
$2p^5$	2_P	$(1+10x)$	$(1+22x)$	$(1-2x)$



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