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THE PERTURBATIONS IN THE HELIUM BAND SPECTRUM

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Abstract

The helium bands furnish an extensive material for the study of perturbations in particular for a test of the theoretical conditions, which according to Kronig must be fulfilled in order that a perturbation may occur. It was found that: I. Whenever two energy levels come close together which satisfy those conditions, a perturbation occurs. II. For those perturbations which cannot be traced to the coincidence of two known terms it can be shown that there must be as yet empirically unknown levels with the required properties to produce these perturbations. III. Whenever two levels come close together which do not satisfy Kronig's conditions, no perturbation occurs.—The nature of the observed perturbations is discussed. Only one term of each sequence is perceptibly perturbed, but at least in one case it can be clearly seen that all the levels after the perturbations are displaced by a constant amount with respect to those before the perturbation. It is also shown how the intensity anomalies may be explained.

SINCE the early days of spectroscopy it has been known that in the regularly spaced sequence of lines in a band sometimes one or more lines are displaced irregularly. The rotational energy levels which give rise to these lines are said to show *perturbations*, and since the beginning of a theory of molecular spectra the reason for these perturbations has been assumed to be some kind of resonance effect within the molecule. Kronig[1] gave more precision to this idea and derived the conditions under which perturbations may occur.

The aim of the present paper is to study the perturbations in the He_2 spectrum and investigate, how far the theoretical rules are able to account for the observed perturbations. The helium band spectrum is particularly well adapted for this purpose as it is well analyzed and contains a large number of electronic levels, the nature of which is fully understood. One example of an interpretation of a perturbation was given previously.[2] In the meantime two papers by Rosenthal and Jenkins[3] appeared in which perturbations in the CO and CN molecule were analyzed in connection with the theory. The authors found a complete agreement with the theory, but their considerations, although doubtless correct in all main points, do perhaps not seem quite conclusive, for in CO the nature of the second electronic level seems doubtful,[4]

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[1] R. de L. Kronig, Zeits. f. Physik **50**, 347 (1928).

[2] G. H. Dieke, Nature **123**, 446 (1929).

[3] J. E. Rosenthal and F. A. Jenkins, Proc. Nat. Acad. **15**, 381 (1929); **15**, 896, (1929).

[4] The authors assume the level which perturbs the final state of the Angstrom bands which are singlets to be the final (triplet) state of the 3rd positive group of CO. That a triplet state perturbs a singlet state to such a degree seems from theoretical reasons highly improbable. There may be however exceptions from the rule which forbids such interaction, but we would expect them to any marked extent only for heavy molecules in which the triplet separation is

and in CN it is a level which is not well known yet. The situation is much clearer for the helium bands, but, as the perturbations take in the CO and CN molecules a form different from that in the helium bands, Rosenthal and Jenkins were able to investigate phases of the problem, for which the He_2 perturbations are unsuited.

The material for the present investigation is taken mainly from the published data of the helium bands, though to a lesser extent also unpublished material[5] in the possession of the author was used.

In order that a perturbation can arise for a given rotational level of the molecule, it is necessary that there is another energy level of the molecule very close to it. The closeness of the two levels is, however, not sufficient for them to perturb each other. According to Kronig they must satisfy besides the following conditions:

A. The total angular momentum J of the two levels must be the same. *B*. Both levels must be positive, or both must be negative.[6] *C*. If the component of the angular electronic momentum along the internuclear axis is Λ for the one level it must be Λ or $\Lambda \pm 1$ for the other one.[7] *D*. The multiplicity of both levels must be the same. *E*. Both levels must be either antisymmetrical or both must be symmetrical in the nuclei if the molecule has two identical nuclei. *F*. The internuclear distance for both levels must be roughly the same.

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considerable. I hope that a further investigation of the CO spectrum which was started in this laboratory will clear up this point.

[5] The analysis of the different He_2 bands has been published very irregularly by different authors in different periodicals. In order to facilitate looking up the original data for those who desire to do so, a table is given here in which is indicated where the different bands can be found. The symbols refer to the following publications:

I.	G. H. Dieke, T. Takamine, S. Suga, Zeits. f. Physik **49,** 637 (1929).
II.	G. H. Dieke, S. Imanishi, T. Takamine, Zeits. f. Physik **54,** 826 (1929).
III.	G. H. Dieke, S. Imanishi, T. Takamine, Zeits. f. Physik **57,** 305 (1929).
C I.	W. E. Curtis, Proc. Roy. Soc. **A101,** 38 (1922).
C III.	W. E. Curtis and R. G. Long, Proc. Roy. Soc. **A108,** 513 (1925).
C IV.	W. E. Curtis, Proc. Roy. Soc. **A118,** 157 (1928).
C V.	W. E. Curtis and A. Harvey, Proc. Roy. Soc. **A121,** 381 (1928).
C VI.	A. Harvey, Proc. Roy. Soc. **A125,** 484 (1929).
Im I.	S. Imanishi, Sc. Papers, Inst. Phys. Chem. Res. **10,** 193 (1929).
Im II.	S. Imanishi, Sc. Papers, Inst. Phys. Chem. Res. **10,** 237 (1929).
Im III.	S. Imanishi, Sc. Papers, Inst. Phys. Chem. Res. **11,** 139 (1929).
P.	E. A. Pestel and W. Weizel, Zeits. f. Physik **56,** 197 (1929).
W I.	W. Weizel and Chr. Füchtbaur, Zeits. f. Physik **44,** 431 (1927).
W II.	W. Weizel, Zeits. f. Physik **51,** 328 (1928).
W III.	W. Weizel, Zeits. f. Physik **52,** 175 (1928).
W IV.	W. Weizel, Zeits. f. Physik **54,** 321 (1929).

Many bands were published in different places. In that case usually only the results of Dieke, Imanishi and Takamine are given because they are probably a little more complete and based on somewhat more accurate measurements. Only for the results contained in Imanishi's papers also another reference is given, if possible, because those papers will probably be inaccessible to many readers.

The author is at present engaged in a complete revision of the whole He_2 band spectrum, but it will take probably some time before it is finished and can be published.

In this paper we shall try to find out from the empirical energy levels of the He_2 molecule whether these conditions are necessary and sufficient to produce perturbations. It is most convenient to divide the investigation into three parts, i.e. I. Find pairs of levels for which the conditions *A* to *F* are satisfied and show that they are perturbed. We shall see that we can find three such pairs of levels and that all of them show pronounced perturbations. II. See whether all the known perturbations (those which were not treated in part I) can be explained by an interaction of two such levels which satisfy the conditions *A* to *F*. This question can also be answered in the affirmative.

Bands	Old notation	Triplet system (Orthohelium)				Singulet system (Parhelium)			
		0→0	1→1	0→1	1→0	0→0	1→1	0→1	1→0
$2s\Sigma \leftarrow 3p\Pi$	$2s-3p$	C III	I	I	I*	C III Im II	Im II W IV	Im II, W IV	†
$4p\Pi$	$4p$	C III	I	I	**P	C III		I	W III
$5p\Pi$	$5p$	C III; Im I	Im I, P	Im I, P	Im I†	P			
$6p\Pi$	$6p$	C III; Im I	Im III, P			P			
$7p\Pi$	$7p$	"	Im III, P			Im I			
$8p\Pi$	$8p$	"	Im III			Im I			
$9p\Pi$	$9p$	"	Im III						
$10p\Pi$	$10p$	"							
$2p\Pi \leftarrow 3s\Sigma$	$2p-3s$	III	I			I			
$4s\Sigma$	$4s$	III	I			W II			
$5s\Sigma$	$5s$	III							
$6s\Sigma$	$6s$	III							
$3d\Sigma$	$3z$	I		W IV		I			
$3d\Pi$	$3x, y$	I		W IV		I	P		
$3d\Delta$	$3d$	C I				II	P		
$4d\Sigma$	$4z$	I	W III	II					
$4d\Pi$	$4x, y$	II	II††	W IV					
$4d\Delta$	$4d$	II	II				C VI		
$5d\Sigma$	$5z$	III					II		
$5d\Pi$	$5x, y$	III					II		
$5d\Delta$	$5d$	III					II		
$6d\Sigma$	$6z$	W III							
$6d\Pi$	$6x$	II §							
$6d\Delta$	$6d$	III							
$3p\Sigma \leftarrow 4s\Sigma$	$2s'-4s$	III							
$5s\Sigma$	$5s$	III							
$6s\Sigma$	$6s$	III							
$4d$	$4d$	III							
$5d$	$5d$	III							
$6d$	$6d$	III							

* Also 1→2 and 2→2 in I.
** Also 1→2 in I.
† Also 2→2 in Im II.
†† Only $2p-4x$.
§ Only $2p-6d_b$.

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[6] Kronig uses the terms even and odd instead of positive and negative. The meaning is that the ψ-function of a positive level remains unchanged if the coordinates of all the particles are replaced by their negative values. For a negative level the sign changes with such a substitution.

[7] The notation in this article is in accordance with the one agreed upon by most workers in band spectra (see Mulliken, Phys. Rev. **36**, 611, 1930). The known energy levels of the He_2 molecule can be considered to arise from one valence electron. The azimuthal quantum number of this electron is indicated by a letter *s*, *p*, *d* the total quantum number by a number preceding this letter, e.g. 5*p*. All the terms e.g. of the 4*d* electron are said to form a term complex. The projection of the orbital momentum on the internuclear axis is designated in the usual way by capital Greek letters Σ, Π, Δ . . . . These symbols are used here to identify the levels also, when on account of the uncoupling of the orbital momentum they have no longer any physical significance.

III. It is to be shown, that whenever two levels coincide closely, which do not satisfy the conditions A to F, no perturbations arise. The He_2 spectrum furnishes ample material to test also this point.

Part I

In Fig. 1 all the known electronic levels of the triplet system of the He_2 molecule are drawn. In order to be able to draw the figure on a large enough scale, the three lowest levels $2s\Sigma$, $2p\Sigma$, $2p\Pi$ are omitted. The term system of the singlet system is exactly analogous, but as it is known with less completeness, we shall leave it mostly out of consideration. For each electronic and vibrational level the rotational levels[8] up to about $J=25$ are known, and our first intention is to find those rotational levels which according to the rules mentioned above are able to perturb each other.

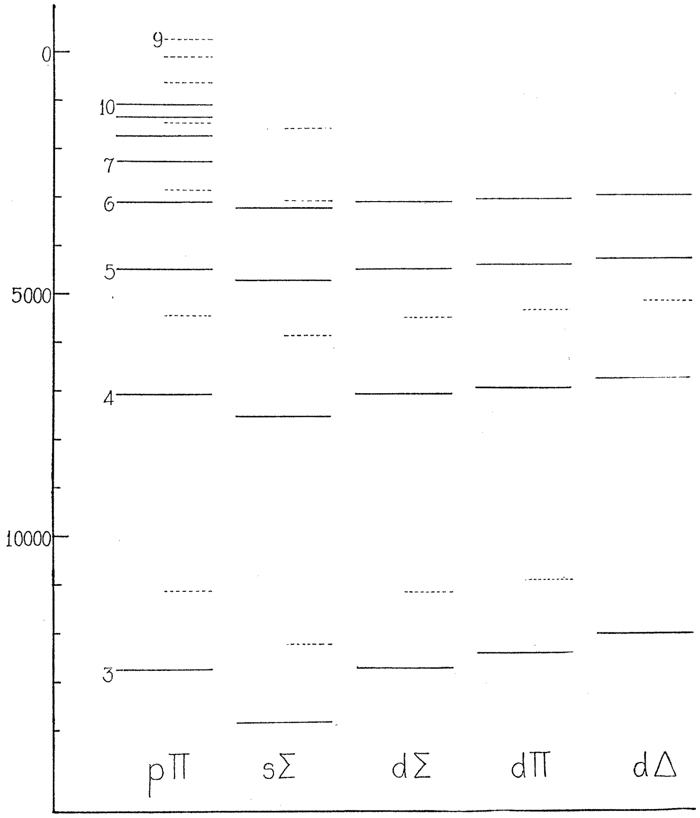

Fig. 1. Diagram of the known triplet levels of the He_2 molecule. The levels represented are those with the lowest rotational quantum number. The drawn out lines are the levels with the vibrational quantum number $V=0$, the dotted ones those with $V=1$.

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[8] For the purpose of the present paper also the triplet system is treated as a singlet system. This is permissible as the triplet separation is very small and cannot be seen under ordinary circumstances. The influence of the spin on the rest of the molecule can therefore be neglected. The quantities which are called f in the present paper refer strictly speaking to K.

The condition E is fulfilled automatically for the levels of the He_2 molecule, as only levels which are symmetrical in the nuclei occur.

The internuclear distance for those levels which have not too different vibrational quantum numbers is roughly the same for all terms, so that we can also regard condition F as fulfilled.

According to D we have to compare triplet levels only with triplet levels.

Whereas conditions D, E and F are fulfilled for any pair of levels of the triplet system, our choice is considerably limited by the condition B.

All the rotational levels can be divided into two classes, the positive and the negative levels. Ordinary transitions occur only between positive and negative levels, whereas, according to B, positive levels can be perturbed only by positive ones and negative levels only by negative ones. Because half the energy levels are missing due to the symmetry of the He_2 molecule, the division into the two classes is especially simple in our case. Successive levels of one electronic state are alternatively positive and negative but, as for the $s\Sigma$ states only the ones with an odd value of J occur, they are all negative for this electronic state. As all the p-levels ($p\Sigma$ and $p\Pi$) can combine with the negative s-levels they must all be positive. All the d-levels ($d\Sigma$, $d\Pi$ and $d\Delta$) combine with the p-levels and are therefore negative.

We have therefore the negative s- and d-levels which may perturb each other and on the other hand the positive p-levels. A perturbation of a p-level by an s- or d-level or vice versa is, according to B, not possible.

Let us consider the negative levels first. We have not made use of the conditions A and C yet. We would not expect the latter one to hold to any extent for those He_2-terms which, like all the d-levels, show a marked uncoupling of the orbital momentum from the internuclear axis. But it turns out that levels which obey the other conditions and violate only C cannot be found among the known levels anyway. Our task has reduced itself now to finding s- and d-levels with the same value of J which fall close together. If we confine ourselves first to levels with the same total electronic quantum number n, there can be obviously no two s-terms with the same J. There are, however, two or three d-levels with the same J namely a $d\Sigma$, $d\Pi$ and $d\Delta$ for odd values of J and a $d\Pi$ and $d\Delta$ for even values of J. These levels might perturb each other. They do it however in a systematic way and their deviations from the normal energy values are usually not called perturbations, because all of the levels are affected in a regular way.[9]

If we confine ourselves to perturbations in the restricted sense, that means to perturbations which are caused by a more or less accidental coincidence of two levels, there remains only the possibility than an s-level comes very close to a d-level with the same J. Now, as Fig. 1 indicates, for small values of J the s-levels lie below the d-levels. The rotational energy for normal levels like the s-levels is roughly $BJ(J+1)$. The constant B which is connected with the internuclear distance is about the same for the s- and d-levels. Now the d-levels are not normal levels but show very pronounced deviations due

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[9] The anomalies which arise from the interaction of the levels of one complex are treated in detail: Zeits. f. Physik **57**, 71 (1929).

to the uncoupling of the orbital momentum of the electron. Both the $d\Pi_\alpha$ and $d\Delta_\alpha$ levels[10] which might be perturbed by an s-level increase more strongly with J than a normal level. Therefore, if for small values the s-levels lie below the $d\Pi$ and $d\Delta$ levels with the same value of J they will do so even more for high J-values. There is, therefore, no chance of a perturbation. There remains finally to compare the s-levels with the $d\Sigma$ levels. Here indeed we find, as the $d\Sigma$ levels increase more slowly with J than normal levels[11] that for a given value of J the corresponding $s\Sigma$ and $d\Sigma$ levels come very close together.

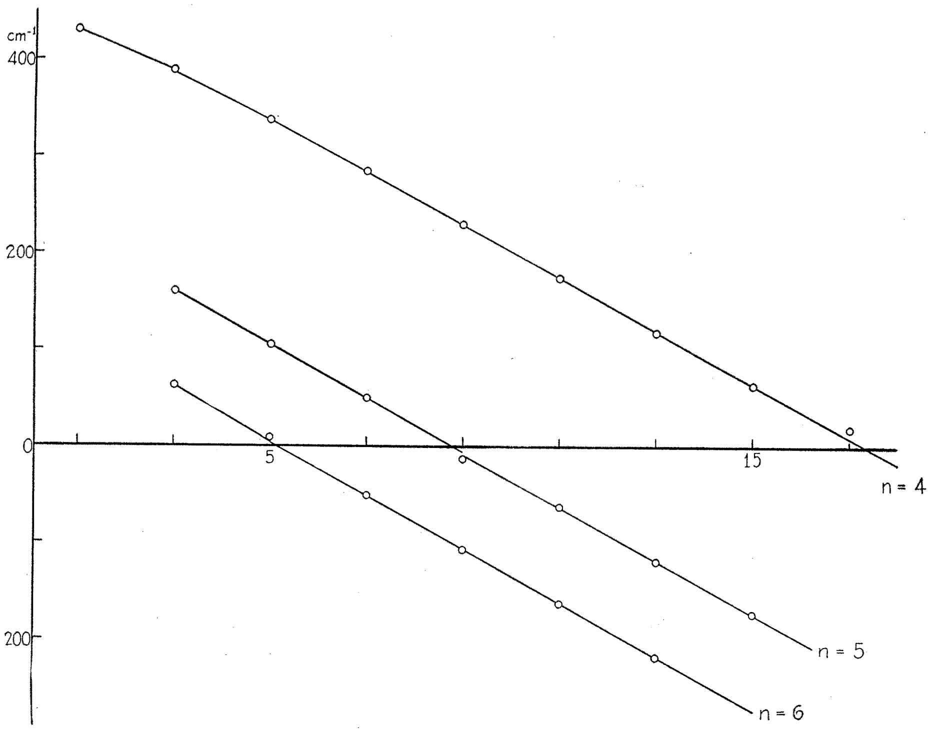

Fig. 2. The difference $nd\Sigma J - ns\Sigma J$ as function of the rotational quantum number J, for $n=4$, 5 and 6.

In Fig. 2. this is illustrated graphically. The difference between the $nd\Sigma -$ and the corresponding $ns\Sigma -$ level is plotted as a function of J for the levels with the total electronic quantum number $n=4$, 5, 6. From the figure can be seen that this difference becomes very small for $J=17$, if $n=4$, for $J=9$ if $n=5$, and for $J=5$ if $n=6$.

Until now we considered only levels with the same total quantum number

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[10] The subscript a and b have here the same meaning as in the previous publications of the author on the helium spectrum. a designates the sublevel which has only odd values of J,b the one with only even values of J. For a symmetrical molecule, like the helium molecule this notation is often more convenient than the notation proposed by Mulliken, Rev. of Modern Phys. **3**, 94 (1931).

[11] The rotational energy is for large values of J proportional to $(J-2)$ $(J-1)$.

n and the vibrational quantum number V zero. We must, however, also expect that levels with $V=1$ and $V=0$ perturb each other. As far as the p-levels are concerned, it happens that there are no levels with the same J of this type which come close together. The perturbations of the p-levels which Curtis and Long found must therefore be due to other reasons, and they are discussed in Part II.

As for the s- and d-levels there are probably a few perturbations but the empirical material is at present not quite sufficient to find them definitely. In one example the position of both levels is known. It is the perturbation of the $4s\Sigma^1$ and $4d\Sigma^1$ levels.[12] The difference between corresponding levels is about $+33$ cm^{-1} for $J=15$ and -20 cm^{-1} for $J=17$. The closest approach of these two electronic levels occurs at the same value of J as for the corresponding levels with $V=0$. But the distance is much larger, 20 cm^{-1} for $V=1$ as compared with 9.9 cm^{-1} for $V=0$ and the corresponding perturbation ought to be accordingly much smaller. The data do not allow to see clearly whether the perturbation is present, as the lines in the $4s\Sigma^1 \rightarrow 2p\Pi^1$ band in which such a perturbation might be detected most easily fade out before reaching the value $J=17$ for the initial state.

The empirical material is entirely absent for finding the analogous perturbations in the corresponding levels with the total quantum numbers five or six.

Fig. 1 shows that the $5s\Sigma^1$ level is very close to the $6d^0$ levels. The same is true for the $5d\Sigma^1$ and $5d\Pi^1$ levels which are not shown in the figure, but the position of which may be estimated from the relative positions of the corresponding levels with $V=0$. This coincidence ought to give rise to some interesting perturbations, but unfortunately the levels are not sufficiently enough known yet.

Description of the perturbations.

$n=4$. The extrapolated difference between $4d\Sigma 17$ and $4s\Sigma 17$ is 9.9 cm^{-1}. This extrapolation cannot be done with a very high degree of precision as the $d\Sigma$ levels follow a rather complicated law. But the use of a more complicated interpolation formula would probably not improve the result much. The value 9.9 cm^{-1} is probably a little too high but can scarcely be more than 1 cm^{-1} wrong. The actually found difference is 18.7 cm^{-1}, so that the distance between the two levels is increased, due to the perturbations by, about 8.8 cm^{-1}. The two levels act as if they repel each other. This behavior is found also in the other two cases, and is in agreement with the theory. The actual perturbations of the $4s\Sigma 17$ term is about -5.1 cm^{-1}, and that of the $4d\Sigma 17$ term $+4.2$ cm^{-1}. These values cannot be obtained with a very high accuracy. Their difference 9.3 cm^{-1} coincides within the limits of an accuracy with the value 8.8 cm^{-1} given above.

$n=5$. Whereas we could extrapolate for the perturbed terms with $n=4$ only from lower values of J, as lines with $J>17$ could not be determined with

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[12] The index at the upper right of the term symbols indicates the vibrational quantum number V. If it is omitted it is usually understoood that we have levels with $V=0$.

certainty, we can extrapolate from both sides of $J=9$ for the terms with the total quantum number five. It is important to note that different results are obtained if we extrapolate from lower or higher rotational terms. This seems to be quite definite and outside the limits of the experimental errors and the errors of extrapolation. The difference $5d\Sigma 9-5s\Sigma 9$ is -6.0 if extrapolated from $J<9$ and -8.6 if extrapolated from $J>9$. The actual perturbed value is -11.4 so that the perturbation is -5.4 resp. -2.8. This difference, if real, can only mean that there is a constant displacement of about 2.6 cm^{-1} in the relative position of all the levels with $J<9$ with respect to all the levels with $J>9$.[13]

That such a thing actually occurs is shown also by the behavior of the $5s\Sigma$ levels alone. All the rotational levels except the perturbed one with $J=9$ can be represented quite with the usual accuracy by the formula $A+BJ(J+1)-\beta(J+\frac{1}{2})^4$. In this formula B and β have the same value before and after the perturbation, but the constant A is 1.06 cm^{-1} higher after the perturbation than before it. That is shown clearly by Table I which gives the differences between successive $5s\Sigma$ levels.

TABLE I.

J	2	4	6	8	10	12	14
$5s\Sigma(J+1)\big\}$ calc.	71.10	127.73	183.92	239.51	294.29	348.08	400.67
$-5s\Sigma(J-1)\big\}$ obs	71.10	127.74	183.88	242.38	292.48	248.16	400.63
obs. − calc.	.00	.01	−.05	2.87	−1.81	.08	−.04

All the observed and calculated differences agree perfectly within the limits of experimental errors except the two values which contain the perturbed term with $J=9$. If only this level were perturbed and all the others normal, then perturbations of the differences $s\Sigma 9-s\Sigma 7$ and $s\Sigma 11-s\Sigma 9$ ought to have the same magnitude and opposite sign. The table indicates that they are 1.06 cm^{-1} different. This means that the $s\Sigma 9$ term is perturbed by $+2.87$ cm^{-1} and that the following levels do not come back to the values which one would expect if there were no perturbations, but are all displaced by the constant amount $+1.06$ cm^{-1}.

An analogous thing seems to be true for the $5d\Sigma$ terms. But as they do not follow a simple formula, it is difficult and uncertain to obtain quantitative data. The term $5d\Sigma 9$ is found to show a perturbation of -2.3 cm^{-1} with respect to the lower levels and of -1.3 with respect to the higher ones. The difference of -1.0 cm^{-1} represents a constant shift of all the higher levels with respect to the lower ones.

$n=6$. The extrapolated difference between $6d\Sigma 5$ and $6s\Sigma 5$ is about $+6.0$ cm^{-1}. (Extrapolation here especially uncertain.) The perturbation of the $6s\Sigma 5$ level with respect to the lower levels is found to be -0.89 cm^{-1} and with respect to the higher levels -1.16 cm^{-1}. There would therefore be a constant shift of -0.27 cm^{-1} of the higher levels with respect to the lower ones. Whether this is real or not cannot be said with absolute certainty. The $6d\Sigma 5$

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[13] Such a behavior was also found by Rosenthal and Jenkins for CO.

level shows a perturbation of +1.5 with respect to the higher levels. Whether there is also a constant shift cannot be made sure of here because there is only one level known below the perturbed one.

Intensities. Until now only the shift of the energy levels has been discussed. But it is found that also the intensities are abnormal. That would mean theoretically that also the characteristic functions of the levels, by which the intensities are determined undergo perturbations. No calculations have been made yet about the amount of the perturbations in the ψ-functions, and they will be in general quite complicated.

An example which does not quite refer to the present case, and which is very much simplified, will give, however, an idea of how the intensities can be affected. The perturbations are due to a quantum mechanical resonance phenomenon. If ψ_1 and ψ_2 are the characteristic functions of two coinciding energy levels, if they do not perturb each other, then very often the perturbing interaction is of such a nature, that the two original states lose their identity and we have to take as the two new characteristic functions $\phi = (\psi_1+\psi_2)/2^{1/2}$ and $\phi_2 = (\psi_1-\psi_2)/2^{1/2}$. The transition probabilities are given by integrals of the form $A_1 = \int x\psi_1\psi dv$ and $A_2 = \int x\psi_2\psi dv$. These would determine the intensity if there were no perturbation. For the perturbed lines the intensity is given by

$$\bar{A}_1^2 = (A_1 + A_2)^2$$

$$\bar{A}_2^2 = (A_1 - A_2)^2.$$

As mentioned above, we cannot expect this simple model to represent the case we are considering here. But it is interesting to note, that a behavior of the intensities as suggested by these considerations can be found in the perturbed lines.

From the experimental point of view the two clearest cases are in the bands $5d\Sigma$ resp. $5s\Sigma \rightarrow 2p\Sigma$ and $6d\Sigma$ resp. $6s\Sigma \rightarrow 2p\Sigma$ because the region in which these bands lie is relatively free from other lines. The intensities of the perturbed lines are

		$n=5$	$n=6$
$ns\Sigma \rightarrow 2p\Sigma$	P:	normal	normal
	R:	very weak	stronger than normal
$nd\Sigma \rightarrow 2p\Sigma$	R:	stronger than normal	weak

The intensities are only roughly estimated but especially the fact that the lines $R(8)$ of $5s\Sigma \rightarrow 2p\Sigma$ and $R(4)$ of $6d\Sigma \rightarrow 2p\Sigma$ are much weaker than normal is quite evident.

Normally i.e. without a perturbation, the P-branch of the combinations with the $d\Sigma$ levels is entirely absent,[9] whereas the R-branches of the combinations with the $s\Sigma$ and $d\Sigma$ levels have intensities of the same order of magnitude.

If we consider therefore the *perturbed* transitions we ought to find one strong and one weak R line (we have strictly speaking no more the right to say which one comes from the $s\Sigma$ and which one from the $d\Sigma$ level) corresponding to the cases $\psi_1+\psi_2$ and $\psi_1-\psi_2$ of our model. That is exactly what we find and the weak line is in both cases the violet component.

The two P-lines ought to have the same intensity (half of the normal of the P line of the $s\Sigma \rightarrow p\Sigma$ transition). That we find only one line with normal intensity shows that the model cannot give an accurate account of the facts, and this cannot be expected, as clearly there is in our case, when the unperturbed levels do not exactly coincide still sense in keeping the $d\Sigma$ and $s\Sigma$ levels separate.

Only by a more detailed calculation we can hope to clear up these points sufficiently.

About the intensities in the other bands, very little definite can be said. They all lie in a region which is very rich in other lines, so that many superpositions may be expected. The only case in which an intensity anomaly seems to be without question is the line $P(10)$ of $5s\Sigma \rightarrow 2p\Pi$ which is weak.

PART II

In the preceding section we have investigated all the perturbations which arise from the interaction of known terms. There are, however other perturbations which were already discovered by Curtis and which cannot arise from any known terms. This section is concerned with a discussion of these perturbations.

They are

$$4p\pi 6 \quad -1.02$$

$$4p\pi 9 \begin{cases} -2.03 \\ +4.43 \end{cases} \text{also perturbed if } V = 1$$

$$5p\pi 2 \quad -1.56$$

$$5p\pi 5 \begin{cases} +1.27 \\ -2.27. \end{cases}$$

We have seen that a p-level cannot be perturbed by an s- or d-level. It might, however, be influenced by another p- or an f-level. We can dispose of the first possibility immediately. For a p-level which might affect $4p\Pi$ could be either a $p\Pi$ level with a higher oscillational quantum number, or a $p\Sigma$ level. It can be easily seen that a $p\Pi$ level with a higher value of V cannot produce such a perturbation. In our case it would have to be $3p\Pi^4$. The extrapolated position of this level is too high to cause the perturbation, but as we cannot be very sure about the extrapolation, this argument is not sufficient. It is very unlikely that two terms of the He_2 molecule with a difference of four units of the vibrational quantum number can have any appreciable effect on each other.[14] Furthermore even if the perturbation in $4p\Pi^0$ were caused by $3p\Pi^4$ there would be no reason for the perturbation of the same rotational levels in $4p\Pi^1$. For the difference between $4p\Pi^1$ and $4p\Pi^0$ and that between $3p\Pi^5$ and $3p\Pi^4$ is quite different. Also it cannot be seen that if $p\Pi 6$ is perturbed why not also $p\Pi 7$ rather than $p\Pi 9$. All these arguments practically exclude the possibility of a perturbation of the levels in question by other $p\Pi$ levels.

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[14] That is due to a restriction of which the rule F on page 647 is a qualitative expression. This rule F which was not originally given by Kronig has to the exact quantitative rule which limits the perturbations of two vibrational levels the same relation as the Franck-Condon rule to the exact rule for the intensities of vibrational transitions.

A $p\Sigma$ level is entirely out of the question, for it contains only rotational terms with an even J and would therefore be unable to perturb $p\Pi 9$.

The only possibility, therefore, at least if we restrict ourselves to the terms of the single valence electron, is that the $p\Pi$ terms are perturbed by f-terms. An f-complex would consist of $f\Sigma$, $f\Pi$, $f\Delta$, and $f\phi$ terms. We cannot expect it to combine with the $4s$-levels. In atoms such a transition would be entirely forbidden (the azimuthal quantum number of the valence electron would change three units), and as the levels of the He_2 molecule, especially the higher ones are very much like atomic levels, we expect this to hold also for the molecular terms. The f-complex ought to combine freely with the d-terms, but these lines would all fall into the infrared. For these reasons the f-complex is not known empirically and we do not know its exact structure, e.g. we do not know whether it is a regular complex, like the d-complex, or an inverted complex like the p-complex. If it is a regular complex and it lies for small rotations a little above the $p\Pi$ level, the $f\Sigma_b$ and $f\Pi_a$ levels would just have the required properties to account for the observed perturbations. But we should expect then a perturbation for a higher $p\Pi_b$ level due to $f\Pi_b$ which has not been found.

It is perhaps better to postpone the discussion of other possibilities until more about the structure of the f-complex is known.

The fact that instead of the one unperturbed line we get two lines if $4p\Pi 9$ or $5p\Pi 5$ are the initial levels was explained previously by the author as being due to a splitting up of the spin fine structure which is usually too narrow to be noticed.

There is, however, another explanation which seems more likely now. Ordinarily only the $p\Pi$ levels and not the f-levels will combine with the $2s\Sigma$ terms. As we saw previously, however, if those levels perturb each other, they lose their identity and we ought to expect both of the perturbed lines to combine with the s-level. The sum of the intensities of the two lines ought to be equal to the expected intensity of the unperturbed line. That was noticed to be the case by Curtis. Whether this is the right explanation for the existence of the two lines can best be ascertained by a further study of similar cases.

PART III

It was shown in Part I that whenever levels which satisfy the conditions of page 647 almost coincide a perturbation results. It remains to be shown that the coincidence of levels which do not satisfy those conditions does not result in a perturbation. With the material at our disposal, of course, no rigorous proof can be given, but the evidence for the correctness of the statement is very strong. We shall try to look first for almost coinciding levels in which only one of the conditions is violated. We can determine the relative position of levels with different degrees of accuracy. All the levels, e.g. of the triplet system belong to two groups. It is possible to determine the relative position of any two levels within one group with the accuracy of the wave-length measurements, whereas the determination of the relative position of two levels belonging to the two different groups involves the calculation of the head of a Rydberg series and is accordingly less accurate. The same is true for two levels, one of which belongs to the triplet and the other one to the singlet system. The two groups are

$$2s,\ np(n \geqq 3);$$

and

$$2p,\ nd(n \geqq 3).$$

The two groups might be connected by the discovery of a band which corresponds to the transition from a level of one group to one of the other group. Such a band would be e.g. $2p\Sigma \rightarrow 2s\Sigma$ which must be expected in the near infrared.

We first look for levels which do *not* satisfy condition A. It is easy to find quite a number. A few examples are $6p\Sigma 14$ and $8p\Sigma 1$ difference 2.3, $8p\Pi 8$ and $9p\Sigma 3$ difference 2.8, $4p\Pi^1 11$ and $5p\Pi 3$ difference 2.9, $3d\Delta 14$ and $3d\Sigma 19$ difference 1.4, $5s\Sigma 11$ and $5d\Pi 10$ difference 1.0 etc. In all these cases the levels come much closer together than in Part I, and nevertheless, there is no trace of a perturbation.

If we look for terms which violate only rule B we have to compare terms of the two different groups mentioned above, and it is not possible to fix the relative position of the terms with the same precision as before. The error will, however, scarcely exceed a few wave numbers.[15]

The following examples show that a shift of that amount cannot make any difference in the conclusions. For, while some terms are pushed farther part, others come closer together.

$4p\Pi 14$	and $4d\Pi 14$	difference $-\ 6.2$
$4p\Pi 16$	and $4d\Pi 16$	difference 12.6
$5p\Pi 6$	and $5d6$	difference -11.3
$5p\Pi 8$	and $5d8$	difference $+\ 8.9$

Also in these cases there is no trace of a perturbation.

It was mentioned before that there is no material at present to study the violation of condition C and that we cannot expect to hold it for the He_2-terms anyway.

As the comparison of singlet and triplet levels involves the limit of a Rydberg series of the singlet system which is known with much less accuracy than those of the triplet system, we shall not give the data here which show that also rule D is necessary for perturbations. Even if the error in the relative position of the singlet and triplet terms is considerable, always levels can be found which satisfy all other conditions except D. In no case a perturbation is found.

As both the conditions E and F are automatically fulfilled for all terms of the helium molecule, there is no possibility to test their validity with the material of the He_2 bands.

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[15] The two terms, the relative position of which has to be found from the limits of the Rydberg series are $2s\Sigma = 34301.8$ (calculated by Curtis and Long from the limit of the series $np\Pi \rightarrow 2s\Sigma$) and $2p\Pi = 29530.7$ (calculated by the author from the limit of the $ns\Sigma \rightarrow 2p\Pi$ series). If these terms are extrapolated from the higher members of the $ns\Sigma$ resp. $np\Pi$ term series the values are 34291.2 resp. 29520.3. The extrapolation to the lowest members of a series is also for atomic spectra rather inaccurate. The agreement of the last values to within about 10 cm^{-1} with the other values shows that the levels follow the Rydberg series law very closely.