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[1] J. A. Hornbeck, Phys. Rev. 84, 615 (1951).

[2] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) A144, 188 (1934).

[3] A. M. Tyndall and C. F. Powell, Proc. Roy. Soc. (London) A134, 125 (1931)

[4] M. A. Biondi and L. M. Chanin, Phys. Rev. 94, 910 (1954).

[5] D. E. Kerr and C. S. Leffel, Bull. Am. Phys. Soc. 7, 131 (1962).

[6] E. C. Beaty and P. L. Patterson, Phys. Rev. 137, A346 (1965).

[7] H. J. Oskam and V. R. Mittelstadt, Phys. Rev. 132, 1435 (1963).

[8] J. M. Madson, H. J. Oskam, and L. M. Chanin, Phys. Rev. Letters 15, 1018 (1965).

[9] E. C. Beaty, J. C. Browne, and A. Dalgarno, Phys. Rev. Letters 16, 723 (1966).

[10] P. L. Patterson, J. Chem. Phys. 48, 3625 (1968).

[11] E. E. Ferguson, D. B. Dunkin, F. S. Fehsenfeld, and A. L. Schmeltekopf, Bull. Am. Phys. Soc. 13, 212 (1968); C. P. de Vries and H. J. Oskam, Phys. Letters 29A, 299 (1969); J. B. Gerado and M. A. Gusinow, Bull. Am. Phys. Soc. 15, 417 (1970).

[12] G. W. Wannier, Bell System Tech. J. 170, 84 (1952).

[13] L. S. Frost, Phys. Rev. 105, 354 (1957).

[14] S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge U. P., New York, 1960).

[15] A. Dalgarno, M. R. C. McDowell, and A. Williams, Phil. Trans. Roy. Soc. London A250, 411 (1958).

[16] L. M. Chanin and M. A. Biondi, Phys. Rev. 106, 473 (1957).

[17] O. J. Orient, Can. J. Phys. 45, 3915 (1967).

[18] A. S. Dickinson, J. Phys. B 1, 387 (1968).

[19] N. Lynn and B. L. Moiseiwitsch, Proc. Phys. Soc. (London) A70, 474 (1957).

[20] A. M. Tyndall and A. F. Pearce, Proc. Roy. Soc. (London) A149, 426 (1935).

[21] A. S. Dickinson, J. Phys. B 1, 395 (1968).

[22] T. Kihara, Rev. Mod. Phys. 25, 844 (1953).

[23] P. Langevin, Ann. Chem. Phys. 8, 245 (1905); see also Appendix II of E. W. McDaniel, *Collision Phenomena in Ionized Gases* (Wiley, New York, 1964).

[24] A. Dalgarno, Phil. Trans. Roy. Soc. London A250, 428 (1958).

[25] E. A. Mason and H. W. Schamp, Ann. Phys. N. Y. 4, 233 (1958).

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Origin of Spectral-Line Satellites

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It is pointed out that the phenomenon of satellites of spectral lines is attributable to the breakdown of the Born-Oppenheimer approximation in the upper state of the collision-pair molecule owing to the proximity or crossing of molecular potential curves of the same symmetry. The Fano treatment of the configuration interaction between a single bound level and a continuum in conjunction with certain simple models for the potential curves yields an analytical expression for the intensity in the near wing of the spectral lines. The distant blue satellites may be shown to arise from the interaction with a second bound vibrational level. Combinations and variations of these two possibilities lead to cases typical of those which have been observed.

I. INTRODUCTION

A great many if not all of the subsidiary maxima associated with various spectral lines[1-3] and generally referred to as "satellites" are directly attributable to the breakdown of the Born-Oppenheimer approximation in at least one of the states, most often an upper state, of the collision-pair diatomic molecule which emits the perturbed spectral line. We have pointed this out briefly in an earlier communication[4]; it is our intention to discuss this process further in the present paper.

The Jablonski theory,[5] which provides admirable insight into the phenomena associated with certain spectral-line-broadening situations, considers the emitter-perturber pair as making up a diatomic molecule, the broadened spectral line emitted by this complex then constituting an analogy to an electronic-vibrational band system. Thus, the intensities in the spectral line will be proportional to the square of the matrix element of the electric dipole moment between the continuous electronic-vibrational states associated with the radiant transition. Such a model will lead to an intensity distribution containing satellites when two or more neighboring or intersecting potentials of the same symmetry are associated with the upper state. Such close approaches are, of course, tantamount to the breakdown of the Born-Oppenheimer approximation. (Combinations of attractive and repulsive potentials of the same symmetry can lead to the same result.) The intersecting curves incidentally lead to composite potentials with double minima of the type postulated by Jefimenko[3] in his quantitative study of satellites using a classical statistical theory.[6] In any event, the configuration interaction method developed by Fano[7] for the treatment of auto-ionization is admirably suited to the description of the effects of this Born-Oppenheimer breakdown on the spectral line. The plan of this paper is as follows.

In Sec. II we discuss an example of our postulated pair of neighboring potentials, then briefly review the terms which are reintroduced into the Hamiltonian by the resulting interaction and the Fano treatment of the configuration mixing thus induced. In Sec. III we delineate the potential and wave-function models which we utilize in order to obtain our analytic expression for the intensity distribution in the perturbed spectral line at frequencies close to the unperturbed line position when we suppose this unperturbed position to corespond roughly to a perturbed bound level. Section V is concerned with the configuration mixing of the vibrational continuum with two bound levels, the more distant of these two corresponding to the violet satellites. In Sec. V we point out certain variations on these two basic themes which have been observed, while in Sec. VI we indicate the sort of density dependence for the violet satellite which has recently been observed. Section VII indicates theory agreement with two miscellaneous observations.

II. CURVE PROXIMITY AND CONFIGURATION INTERACTION

The spectral lines emitted by the alkali, cesium, provide familiar examples of the satellite phenomenon when perturbed by the presence of noble-gas atoms such as argon. The second doublet of the principal series of cesium arises from transition having the pair of upper levels $7p\,^2P_{1/2,3/2}$.[8] Since the collision partner is a noble-gas atom, we shall assume it to be in its ^1S state. Therefore, the Wigner-Witmer[9] product rules tell us that the diatomic molecule formed by this collision pair will have the states $^2\Sigma^+$ and $^2\Pi$ when Hund's coupling case *a* is assumed. Cesium has a $6d\,^2D$ level some 600 wave number above its $7p\,^2P$ which, would, in the isolated case, have nothing to do with the resonance doublet. When a collision occurs with another atom in a ^1S state, however, the $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ diatomic states are formed, and this situation is radically altered. Let us suppose that the ^2D: $^2\Sigma^+$ state is attractive. Then we shall anticipate its proximity to the ^2P: $^2\Sigma^+$ as indicated schematically in Fig. 1. (We remark that the two $^2\Sigma^+$ curves are not required to intersect in order that the phenomenon which we shall discuss may occur, although such intersection may take place in some physical situation.) Insofar as the wells are concerned, Bernstein and Muckerman[10] tell us that the experimentally determined depth of the Cs-Ar well associated with the ground electronic state is about 50 cm^{-1}. Therefore, the roughly 300-cm^{-1} depth of the upper well indicated here would not appear unreasonable. Obviously, the lower of the two pictured wells could have any depth, even to include zero depth, without affecting our treatment. For reasons which will later be obvious, we have supposed the upper potential well to contain two vibrational levels as is indicated on the figure. Finally, in order to complete our explanation of the figure, we remark that the observations of Gilbert and Ch'en[11] for the Cs-Ar collision pair, for example, were carried out at a temperature of about 440 °K. The mean continous vibrational energy of the CsAr molecule for such a temperature is indicated.

Let us consider the complete wave equation for the CsAr molecule and suppose that the solution may be assumed to be of the product form

$$\Psi_{mk} = \Theta_m R_{mk}/r, \tag{1}$$

where Θ_m is a function of the electronic and nuclear rotational coordinates, and R_{mk} is the discrete or continuous function of the nuclear vibrational coordinates. If we suppose the electronic wave function to be only parametrically dependent on the internuclear separation, the Born-Oppenheimer approximation, as Rice[12] has shown, allows us to neglect the following terms in the Hamiltonian:

$$V\Psi_{mk} = -\frac{\hbar^2}{2m}\,\frac{R_{mk}(r)}{r}\,\frac{\partial^2\Theta_m}{\partial r^2} - \frac{\hbar^2}{m}\frac{1}{r}\,\frac{dR_{mk}(r)}{dr}\,\frac{\partial\Theta_m}{\partial r}\ , \tag{2}$$

where m is the reduced mass of the collision pair.

Now we suppose that, if we carry out the calculation requisite to obtaining an extended configuration-interaction linear-combination-of-atomic-orbitals–molecular-orbital (LCAO-MO) wave function, Fig. 1 will result from taking matrix elements of these electronic wave functions over the Hamiltonian which includes the electronically dependent portions plus the nuclear repulsion. (We assume ground rotational states.) The determination of bound and continous vibrational wave functions for the two potentials completes the calculation under the Born-Oppenheimer approximation. In energy regions such as those corresponding to the

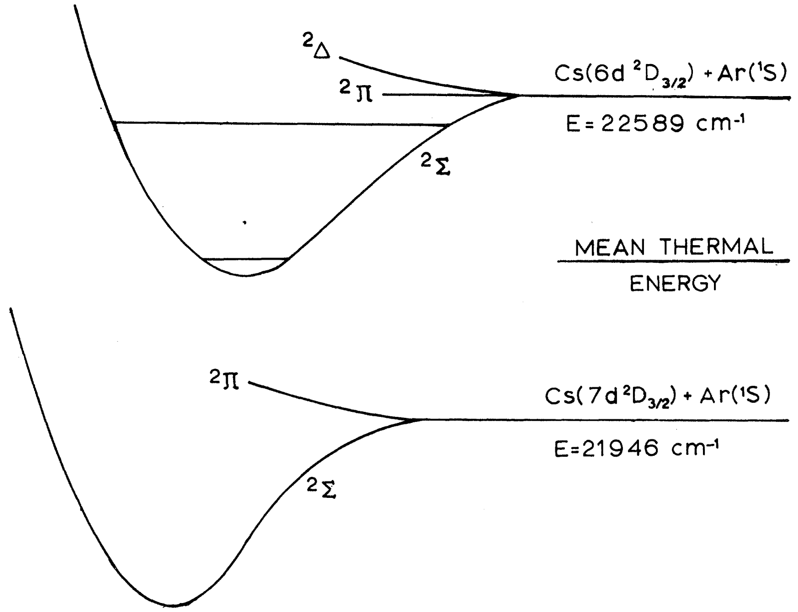

FIG. 1. Schematic representation of the postulated CsAr potentials associated with the $7p\,^2D$ and $6d\,^2D$ states of Cs in the presence of Ar. The mean thermal energy indicated corresponds to a temperature of 440 °K.

"mean thermal energy," this approximation breaks down, however, since electronic-vibrational wave functions must now be combinations of continous functions associated with the lower and bound functions associated with the upper of the two potential curves. The Born-Oppenheimer neglected terms of Eq. (2) provide the perturbing portion of our Hamiltonian while the Fano configuration-interaction approach provides the method for the treatment of the perturbation.

In Sec. II of his paper Fano deals with the situation which we shall first postulate here – one discrete state and one continuum. He begins by assuming that the wave function corresponding to an energy E may be expressed as a linear combination of the wave functions ϕ for the bound state and $\psi_{E'}$ for the continous states:

$$\Psi_E = a\phi + \int dE'\, b_{E'}\psi_{E'} \;. \tag{3}$$

Upon determination of the expansion coefficients, Fano obtains the following expression for the matrix element of an operator T between some initial state i and the configuration mixed state Ψ_E:

$$(\Psi_E|T|i) = \frac{1}{\pi V_E^*}(\phi|T|i)\sin\Gamma + \frac{1}{\pi V^*}P\int dE'\,\frac{V_{E'}^*(\psi_{E'}|T|i)}{E-E'} \times \sin\Gamma - (\psi_E|T|i)\cos\Gamma, \tag{4a}$$

where

$$\Gamma = -\arctan\{\pi|V_E|^2/[E-E_\phi^o - V_{\phi\phi} - F(E)]\} \;, \tag{4b}$$

$$V_{\phi\phi} = (\phi|V|\phi) \;, \quad V_E = (\phi|V|\psi_E) \;, \tag{4c}$$

$$F(E) = P\int dE'\,[|V_E|^2/(E-E')] \;, \tag{4d}$$

where P refers to the principal part.

The Jablonski theory established the proportionality between the intensity distribution in a spectral line and the square of the matrix element of the electric dipole moment for the transition which yields the line. Therefore, the square of the matrix element of the electric dipole moment $(\psi_E|M|i)$ as given by Eq. (4a) will tell us the line profile.

Precise evaluations of the matrix elements of the two terms in Eq. (2) would require precise molecular wave functions, a requirement which seems unlikely to be met in the near future. Therefore, we postulate a constant value for $\partial\Theta_m/\partial r$, an assumption which will surely be true for sufficiently great nuclear separation. Such an assumption will eliminate the first term on the right-hand side of Eq. (2).

III. ANALYTIC LINE WING EXPRESSION (CLOSE IN)

Although it is to be hoped that future studies of this nature will yield a great deal of information about excited-state potentials, such information is presently very meager. It therefore seems most appropriate to use for these potentials the simplest models which are commensurate with an explanation of the phenomenon under consideration. Further, more "realistic" potentials preclude the possibility of obtaining potentially enlightening analytic expressions for the intensity distribution. Therefore, we postulate that (i) the continuum functions are associated with a purely repulsive potential in the form of an infinite barrier, and (ii) the bound functions are associated with an harmonic-oscillator potential.

Mason and Munn[13] have pointed out that, for small kinetic energy, the continuous wave function has the same number of nodes as the "last" bound function in the well. Therefore, we suppose that (iii) the continuum function in the lower state is to be approximated by the last bound function.

We restrict ourselves to the simplest case of a purely repulsive potential, since it yields the salient features of the close-in theory while simplifying as much as possible the algebraic manipulations.

We approximate the continuum function in the lower state by the following function:

$$\psi_i = N_2 \sin[A(r + r_2)]\, e^{-(1/2)\beta[r-r_2]^2}, \tag{5a}$$

where $A = v\pi\beta/9$, and r_2 is simply a parameter for the adjustment of the radial separation between the lower and upper wells. Our continuum function associated with the repulsive upper state may be represented as

$$\psi_E = N(1/k_f r) \sin[k_f(r - r_1)] \;, \tag{5b}$$

where k_f is the wave number corresponding to the continuous vibrational energy while r_1 is the location of the repulsive core.

There will, of course, be certain situations in which $(\psi_E | i)$, and hence the last two terms in Eq. (4a), will contribute something to our overlap integral. This will not be the case, however, when either (i) there are sufficient levels in the lower well so that the oscillation of Eq. (5a) will effectively zero out the integral or (ii) the relative location of the lower well and the upper core have the same result. The possibilities of such cancellation are sufficiently great that we should be able to follow the main features of the phenomenon by assuming that it takes place. Therefore, we require only V_E, that is, the matrix element of the Born-Oppenheimer neglected terms over the upper bound and excited states. From Eqs. (5) this becomes

$$\begin{aligned} V_E &= \text{const} \int e^{-(1/2)\alpha(r-r_e)^2} \cos[k_f(r - r_1)]\, r\,dr \\ &= \text{const} \int e^{-(1/2)\alpha r^2} \cos[k_f r - k_f(r_1 - r_e)]\, r\,dr \\ &= \text{const}\{\cos[k_f(r_1 - r_e)] \int e^{-(1/2)\alpha r^2} \cos(k_f r) r\,dr \\ &\quad + \sin[k(r_1 - r_e)] \int e^{-(1/2)\alpha r^2} \sin(k_f r) r\,dr\} . \end{aligned} \tag{6}$$

If, for reasons which will become apparent in Sec. IV, we choose the normal frequency of our bound molecule as 240 cm^{-1}, the bell portion of the bound function will effectively extend less than 1 Å. Therefore, since $r < 10^{-8}$ while $k_f \sim 300$, Eq. (6) will become

$$\begin{aligned} V_E &= \text{const}\{\cos[k_f(r_1 - r_e)] \int e^{-(1/2)\alpha r^2} r\,dr\} \\ &= \text{const} \times \cos[k_f(r_1 - r_e)] . \end{aligned} \tag{7}$$

Consider Eq. (4b). The unit of this contribution from the integral over the electronic coordinates is reciprocal centimeters, that from the normalizing factor for the continuous functions, the square root of this. We then take the product of these two as of order 10^{12}. If we suppose the denominator of Eq. (4b) to correspond to $(E - E_0)$ in the resulting spectral line, we may then evaluate the remainder of the constants within the arctangent argument. The order of magnitude for $(\omega - \omega_0) \sim 1$ was about 10^{-4} – a rough estimate, but one which should be meaningful for $(\omega - \omega_0)$ not too small. We therefore say that $\sin\Gamma$ merely corresponds to the argument Γ.

Next we note the following relationship between the frequency separation from line center, $(\omega - \omega_0)$, and the various wave numbers:

$$k_f^2 = (4\pi m/\hbar)\,(\nu - \nu_0) + k_i^2 \;, \tag{8}$$

where k_i is the kinetic wave number of the collision in the lower state, k_f the wave number in the upper and m is the reduced mass. We now obtain the following expression for the distribution of intensity in the wings of the spectral line:

$$I = \text{const} \times \cos^2\left[D\left(\frac{4\pi mc}{\hbar}\,(\omega - \omega_0) + \frac{2mkT}{\hbar^2}\right)\right] \Big/ (\omega - \omega_0)^2,$$

$$D = r_1 - r_e \,, \tag{9}$$

where we have identified the lower-state wave number with the temperature T.

It is apparent from the appearance of $(\omega - \omega_0)$ in the denominator of Eq. (9) that we have assumed the center of the observed spectral line to correspond to the position of the perturbed bound vibrational state, that is, $E_\phi + V_{\phi\phi} + F(E)$ in Eq. (4b).

It is also apparent from Eq. (9) that the separation between satellites will tend to decrease with increasing perturber mass. This "bunching" with increasing mass has apparently not been reported in the literature; however, it has been observed by Jefimenko[14] for the resonance doublet of cesium where it is present for the neon, argon, krypton, xenon series of perturbers. This m dependence should not be confused with the Ch'en and Takeo[2] observation of a $m^{-1/2}$ dependence for the separation of the violet satellite from line center. The violet satellite to which they refer is essentially an independent phenomenon which we discuss in Sec. IV.

IV. DISTANT VIOLET SATELLITE

The satellites which are to be anticipated from Eq. (9) will be located within a few units or a few tens of inverse centimeters from the center of the spectral line, and we can associate them with the configuration mixing of a single bound state and various neighboring continuum states. A satellite located several hundred inverse centimeters from the spectral-line center cannot be accounted for by Eq. (9), and such satellites are quite commonly encountered. Gilbert and Ch'en,[11] for example, have recently observed such a satellite at about 240 cm^{-1} separation from the $^2P_{3/2}$ component of the Cs(1)/Ar line.

Such a satellite is readily accounted for by including a second bound vibrational state in our configuration-mixed wave function. In such a situation the intensity behavior near unperturbed line center is controlled by, say, the configuration mixing of the ground vibrational state with the continuum. As we move into the line wing, we are proceeding to energies such that the mixing effect is of little consequence. As our energy continues to increase and as we approach the energy of the first ($v=1$) bound level, however, the mixing effects again begin to make themselves felt, the violet satellite which subsequently appears being roughly a measure of the bound vibrational level separation. Thus, the violet satellite observed by Gilbert and Ch'en would correspond to a level separation of about 250 cm^{-1}. Simply in order to illustrate the increase in intensity which is to be anticipated in the neighborhood of the higher vibrational level, we partially write down Fano's expression for the overlap integral, one of whose states is a configuration mixture of one continuum and several discrete states [Eq. (65)]:

$$(\Psi_E|i) = \cos\Delta \sum_\nu \frac{\tan\Delta_\nu}{\pi V_{\nu E}} (\phi_\nu|i) + \cdots , \tag{10a}$$

$$-\sum_\nu \tan\Delta_\nu = \sum_\nu \pi|V_{E\nu}|^2/(E-E_\nu). \tag{10b}$$

It is obvious that the factor $(E-E_\nu)^{-1}$ will lead to an intensity maximum in the neighborhood of the higher bound vibrational state so we may illustrate by means of Fig. 2.

We presume an absorbing transition. Before the photon is absorbed the energy of the diatomic molecule will correspond to what we have labeled "mean thermal energy." Now let us suppose that the absorption of a photon corresponding to the unperturbed Cs frequency ω_0 results in an excitation to the indicated upper level. We suppose this level to lie close to the lower of the two bound states as shown on the figure. The spectral line which would be observed would correspond to that indicated on the left-hand side of the figure except, of course, there would be a certain amount of structure superposed on the intense component as indicated by Eq. (9) – structure which, however, might not be observed because of a rapid decrease in intensity.

V. SATELLITES AND CONTINUUM FLUCTUATIONS

In Sec. III we have considered a physical situation which would probably result in several subsidiary maxima to the red side of and close to the line center. We have tacitly assumed in that section that the resonance of, say, Eq. (4b) corresponds to line center and that the phenomena under consideration are attributable to the configuration interaction of the continuum with a close-lying bound state. In Sec. IV we have considered the physical situation which would arise as a result of configuration interaction with a more distant bound state. Experiments, both reported and unreported, have provided the variations on these basic themes.

Case A. The first case is that of two or more close-in satellites or "fluctuations of the continuum" as they have been termed by Jefimenko and Curtis.[15] This is precisely the situation discussed in Sec. III.

Case B. The second is a single close-in red satellite and a distant blue satellite. The resonance denominator of Eq. (4b) now corresponds to the red satellite, the intensity decrease at greater (red) separations from line center effectively masking any additional structure. The blue satellite arises precisely as discussed in Sec. IV.

Case C. The third is a comparatively distant red satellite on which is superposed a number of continuum fluctuations. This is a combination of Secs. III and IV, the red satellite arising from the interaction with a relatively distant but lower-energy bound level for which a treatment of the type of Sec. III will provide structure.

These are the basic cases which have been observed, but the reader will readily note the possibilities for the existence of various other but analogous cases.

VI. DENSITY DEPENDENCE OF SATELLITE DISPLACEMENT

The dependence of, say, the blue-satellite separation on the perturber density and the fashion in which this dependence varies with variations in perturber density may quite readily be indicated from the theory. Gilbert and Ch'en,[11] for example, detail the separation of the violet satellite from line center for perturbation of the $^2P_{3/2}$ component of Cs (1) by Ar. The separation dependence on perturber density appears to be independent of density to relative densities of fifty or so; it could be linear in the region of slightly higher relative density, and appears to be roughly quadratic for still higher densities, the authors following the

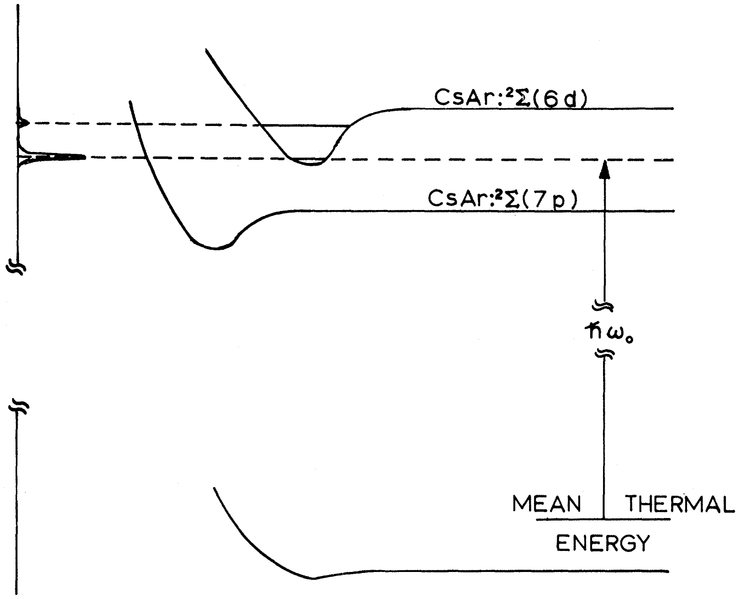

FIG. 2. Schematic representation of the potentials involved in producing the satellites associated with the second member of the cesium principal series. ω_0 is the unperturbed spectral-line frequency.

displacement of the satellite to relative densities of about 160. In order to account for such behavior qualitatively, let us consider two bound vibrational states interacting with our vibrational continuum. If we suppose one of these states to correspond roughly to line center, an increase in separation between them will correspond to the shift of the violet satellite. Our interest is in the change in separation of the two bound levels as a result of the interaction with the continuum. Here again we are dealing with a situation analogous to that treated by Fano[7] in his Sec. V so that much detail is not called for.

The two bound vibrational levels are perturbed by

$$F_{nm}(E) = P\int dE'\, V_{nE'} V_{E'm}/(E - E'). \qquad (11)$$

We apply ordinary perturbation theory to Eq. (11) in order to obtain the level, and hence satellite separation, in zero, first, and second order:

$$\Delta E^0 = E_2^0 - E_1^0, \qquad (12a)$$

$$\Delta E^1 = F_{22} - F_{11}, \qquad (12b)$$

$$\Delta E^2 = 2F_{21}F_{12}/(E_2^0 - E_1^0). \qquad (12c)$$

It is reasonable to suppose that the continuous wave function utilized in the evaluation of $V_{nE'}$ is normalized to the average volume occupied by a single perturber. Therefore, $V_{nE'}$ is proportional to $N^{1/2}$. Therefore, ΔE^0 is independent of N, ΔE^1 is linearly dependent on N, and ΔE^2 is quadratically dependent on this parameter.

VII. MISCELLANEOUS

Jefimenko[14] has observed the perturbation of Cs (1) by Ne, Ar, Kr, and Xe. It is interesting to note the bunching of continuum fluctuations with increasing mass which is, of course, predicted by Eq. (9).

For the alkali metals, Jefimenko has pointed out that the satellite location apparently bears some relation to the perturber cross section for the scattering of slow electrons, an observation which tends to connect this phenomenon with the Fermi[16] theory for the shifts of the high-series members. That there will be a possible connection may be inferred from Eqs. (5b) and (9). The scattering cross section will be proportional to the sine of the phase shift squared. From Eq. (5b) the phase shift will be $k_f r$, and it is apparent that Eq. (9) may be written so that is contains $\sin^2 k_f r_1$. A relation between satellite position and scattering cross section could thus result. This scattering cross section will be that for the scattering of the noble gas by the alkali; however, for increasing principal quantum number the potential, and hence the scattering situation will more closely correspond to that of an electron and the scattered noble-gas atom. Thus, some relationship, not only between the satellite description and the Fermi model but also between the satellite position and the electron–noble-gas cross section, is to be anticipated.

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[1] S. Y. Ch'en and C. W. Fountain, J. Quant. Spectry. Radiative Transfer 4, 323 (1964).

[2] S. Y. Ch'en and M. Takeo, Rev. Mod. Phys. 29, 20 (1957).

[3] O. Jefimenko, J. Chem. Phys. 39, 2457 (1963).

[4] R. G. Breene, Jr., Acta Phys. Polon. A37, 477 (1970).

[5] A. Jablonski, Acta Phys. Polon. 6, 371 (1937); Phys. Rev. 68, 78 (1945).

[6] R. G. Breene, Jr., *The Shift and Shape of Spectral Lines* (Pergamon, Oxford, 1961).

[7] U. Fano, Phys. Rev. 124, 1866 (1961).

[8] Cf. C. E. Moore, *Atomic Energy Levels*, Vol. III, Natl. Bur. Std., (U. S.) Circ. No. 467 (US G. P. O. Washington, D. C., 1958).

[9] E. Wigner and E. E. Witmer, Z. Physik 51, 859 (1928).

[10] R. B. Bernstein and J. T. Muckerman, in *Intermolecular Forces*, edited by J. O. Hirschfelder (Interscience, New York, 1967).

[11] D. E. Gilbert and S. Y. Ch'en, Phys. Rev. 188, 40 (1969).

[12] O. K. Rice, Phys. Rev. 35, 1551 (1930).

[13] E. A. Mason and R. J. Munn, Am. J. Phys. (to be published).

[14] O. Jefimenko (private communication).

[15] O. Jefimenko and W. Curtis., J. Chem. Phys. 27, 953 (1967).

[16] E. Fermi, Nuovo Cimento 11, 157 (1934).

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Analogy between the Laser Threshold Region and a Second-Order Phase Transition

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An analogy between the laser threshold region and a second-order phase transition is presented. The electric field acts as the order parameter for the laser while the atomic-population inversion plays the role of a temperature. The quantum-statistical theory of a laser including a symmetry-breaking external signal is discussed in order to establish a correspondence with the problem of a ferromagnet (treated in the molecular-field approximation) situated in an externally applied magnetic field. It is demonstrated that the results of the laser analysis may be discussed in terms of an energy function which is similar to the free energy of a thermodynamic system.

I. INTRODUCTION

The quantum theory of a laser oscillator has been the subject of recent theoretical[1] and experimental[2] activity. The problem is basically to understand the nonequilibrium statistical dynamics of the (single-mode) laser field as it interacts with the lasing medium. The physical situation is of a sufficiently complex nature to contain many aspects of a many-body problem, but it is simple enough to permit, to a good approximation, a complete solution. It seems, therefore, attractive to consider the possibility of useful analogies between the laser theory and other problems in nonequilibrium statistical mechanics. In fact, an interesting comparison may be made between second-order phase transitions, such as the order-disorder transitions of ferromagnetic and ferroelectric materials or the vapor-liquid transition of a pure fluid, and the laser near threshold.[3] It is well known, for instance, that the state of a laser changes abruptly upon passing through the threshold point. Furthermore, the laser-field fluctuations and the decay times associated with these fluctuations are much larger in the vicinity of threshold. The purpose[4] of the present paper is to demonstrate that the laser-threshold behavior is very analogous to a second-order phase transition.

The basis for this similarity becomes evident when it is recalled that the usual treatments of laser behavior are self-consistent field theories. In the laser analysis each atom develops a radiating dipole in an electromagnetic field due to (i.e., emitted by) all of the other atoms. The radiation field produced by an ensemble of radiating