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Exciton Theory by Second Quantization¹

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I. INTRODUCTION

The customary procedure in the solution of the exciton problem has been to use the apparatus of the Rayleigh-Schrödinger perturbation theory, while limiting oneself to first-order corrections. Recently another approach, formulated in the language of many-body theory, has been developed and will form the subject of this discussion. The first steps in the evolution of this approach were taken by Fano (1) and Hopfield (2), independently a more extensive and comprehensive treatment has been given by Agranovich (3-6) in the Soviet Union. Since the work of the latter is unfortunately not so familiar to American researchers as it should be, we have felt it desirable to restate here briefly Agranovich's method.

Let us suppose that we have a system of N particles (molecules), each unit being labeled by a site index, s , and possessing a set of energy eigenstates labeled by an index f . We define a set of occupation numbers $N(s_f)$: $N(s_f) = 1$ if unit s is in eigenstate f ; $N(s_f) = 0$ if it is not. The following relations hold logically for a system with a fixed number of units N :

$$\sum_f N(s_f) = 1 \quad \sum_{s,f} N(s_f) = N \quad N(s_f)N(s_g) = N(s_f)\delta_{fg} \quad (1)$$

We now define creation and annihilation operators b^+ , b in the occupation number space in the following manner:

$$\begin{aligned} b_{p_f}^+ C(\dots N(s_g) \dots) &= (1 - N(p_f)) C(\dots (s_g) + \delta_{s_g p_f} \dots) \\ b_{p_f} C(\dots N(s_g) \dots) &= N(p_f) C(\dots N(s_g) - \delta_{s_g p_f} \dots) \end{aligned} \quad (2)$$

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where C is some function of the occupation numbers. This definition of creation and annihilation operators is peculiar to a formulation of excitations and yields the Pauli commutation relations (γ):

$$\begin{aligned} [b_{p_f}, b_{s_g}]_- &= 0 & [b_{p_f}^+, b_{s_g}^+]_- &= 0 & [b_{p_f}, b_{s_g}^+]_- &= 0 \\ [b_{p_f}, b_{p_f}^+]_+ &= 1 & b_{p_f}^+ b_{p_f} &= N(p_f) \end{aligned} \quad (3)$$

In this representation the Hamiltonian

$$H = \sum_p H_p + \frac{1}{2} \sum_{p \neq r} V_{pr} \quad (4)$$

may be written as

$$H = \sum_{p, f, h} \langle f | H_p | h \rangle b_{p_f}^+ b_{p_h} + \frac{1}{2} \sum_{\substack{p & r \\ f, h, g, i}} \langle fg | V_{pr} | hi \rangle b_{p_f}^+ b_{r_g}^+ b_{p_h} b_{r_i} \quad (5)$$

where

$$\begin{aligned} \langle f | H_p | h \rangle &= \int \phi_{p_f}^* H_p \phi_{p_h} d\tau_p \\ \langle fg | H_{pr} | hi \rangle &= \int \phi_{p_f}^* \phi_{r_g}^* V_{pr} \phi_{p_h} \phi_{r_i} d\tau_p d\tau_r \end{aligned}$$

In the exciton problem we assume knowledge of the properties of the isolated units; we are interested in the changes of these properties when the units interact with each other according to V_{pr} . Thus the first term in the Hamiltonian becomes

$$\sum_{p, f} E_{p_f} b_{p_f}^+ b_{p_f} = \sum_{p, f} E_{p_f} N(p_f) \quad (6)$$

A solution of our problem would consist in a reduction of equation 5 to diagonal form:

$$H = \sum_{\eta} E_{\eta} N(\eta) = \sum_{\eta} E_{\eta} \beta_{\eta}^+ \beta_{\eta} \quad (7)$$

where the E_{η} are the fundamental excitations of the aggregate.

The interaction part of equation 5 may be separated into terms with matrix coefficients of the following types:

- (a) $\langle fg | V | fg \rangle$
- (b) $\langle f0 | V | 0g \rangle$ and $\langle 00 | V | fg \rangle$ (8)
- (c) $\langle fg | V | hi \rangle$ 0 = ground state

At this point two simplifications are made by Agranovich. First the interaction of excited states, i.e., term (c), is neglected. Second, in term (a), members quadratic

in $N(p_f)$ are neglected. These simplifications are justified by our interest only in a few of the excited states of the aggregate, and in crystals where the number of units excited at any time is small compared to N . It may be noted that, if we take V as a dipole-dipole interaction, and assume the absence of permanent dipoles in any state, the terms involved in the second assumption vanish.

We next introduce excitons, i.e., operators B^+ , B , which correspond to the creation and annihilation of excitations.

$$\begin{aligned} B_{p_f}^+ &= b_{p_f}^+ b_{p_0} \\ B_{p_f} &= b_{p_0}^+ b_{p_f} \end{aligned} \quad (9)$$

It may be easily verified that

$$\begin{aligned} [B_{p_f}, B_{s_0}]_- &= 0 \\ [B_{p_f}^+, B_{s_0}^+]_- &= 0 \\ [B_{p_f}, B_{s_0}^+]_- &= \delta_{p_f s_0} [1 - 2N(p_f)] \end{aligned} \quad (10)$$

Now the third assumption is made that, since we are working in the low excitation region, the average value of $N(p_f)$ will be small, and we may replace the approximate Bose commutation rule by an exact one. This indeed is the crucial assumption of the theory—one which allows a closed solution of the problem. With these assumptions the Hamiltonian may be rewritten as

$$H = E_0 + \sum_{p, f} \Delta_{p_f} N(p_f) + \frac{1}{2} \sum_{\substack{p \neq r \\ f, g}} \langle 0f | V_{pr} | g0 \rangle (B_{p_0}^+ + B_{p_0}) (B_{r_f}^+ + B_{r_f}) \quad (11)$$

where

$$\begin{aligned} \Delta_{p_f} &= E_{p_f} - E_{p_0} + \sum_r' (\langle 0f | V_{pr} | 0f \rangle - \langle 00 | V_{pr} | 00 \rangle) \\ E_0 &= \sum_p E_{p_0} + \frac{1}{2} \sum_{p \neq r} \langle 00 | V_{pr} | 00 \rangle \end{aligned} \quad (12)$$

The quadratic form in equation 11 may be diagonalized by a canonical transformation (δ, ϑ). The Bose form

$$H = E_0 + \frac{1}{2} \sum_{\alpha, \beta} A_{\alpha\beta} b_{\alpha}^+ b_{\beta}^+ + \frac{1}{2} \sum_{\alpha, \beta} A_{\alpha\beta}^* b_{\alpha} b_{\beta} + \sum_{\alpha, \beta} B_{\alpha\beta} b_{\alpha}^+ b_{\beta} \quad (13)$$

with

$$\begin{aligned} A_{\alpha\beta} &= A_{\beta\alpha} \\ B_{\alpha\beta}^* &= B_{\beta\alpha} \quad [b_{\alpha}, b_{\beta}^+]_- = \delta_{\alpha\beta} \end{aligned}$$

is reduced to diagonal form as a result of the transformation to new Bose operators ξ_ρ :

$$\begin{aligned} b_\alpha &= \sum_\rho (\xi_\rho U_{\alpha\rho} + \xi_\rho^+ V_{\alpha\rho}^*) \\ b_\alpha^+ &= \sum_\rho (\xi_\rho^+ U_{\alpha\rho}^* + \xi_\rho V_{\alpha\rho}) \end{aligned} \quad (14)$$

where U and V are determined from

$$\begin{aligned} EU_\alpha &= \sum_\beta (A_{\alpha\beta} V_\beta + B_{\alpha\beta} U_\beta) \\ -EV_\alpha &= \sum_\beta (A_{\alpha\beta}^* U_\beta + B_{\alpha\beta}^* V_\beta) \end{aligned} \quad (15)$$

with the normalization condition

$$\sum_\alpha (U_\alpha^* U_\alpha - V_\alpha^* V_\alpha) = 1 \quad (16)$$

Solutions exist only for certain $E = E_\rho$, which are the fundamental excitations of the system, since in the new variables

$$H = E_0 - \sum_{\alpha, \rho} E_\rho |V_{\alpha\rho}|^2 + \sum_\rho E_\rho \xi_\rho^+ \xi_\rho \quad (17)$$

For the exciton problem in a molecular crystal, use is made of the translational symmetry; the secular equation is then reduced to order $L \times M$, where L is the number of molecules in a unit cell, and M is the number of excited states for each molecule. No perturbation expansion is required.

II. CRITICAL EVALUATION

Assumptions

The crucial advantage of the method is the casting of excitons as bosons. Not only is the Bogoljubov-Tjablikov canonical transformation apparatus available for diagonalizing the Hamiltonian without the use of perturbation theory, but also the problem is in a form where the consideration of interactions with other boson systems such as phonons or photons is easily accomplished. Historically the study of exciton-photon interactions (1, 2) preceded Agranovich's solution. Similar treatments have been given by Demidenko (10) and Ovander (11), the latter concentrating on the Raman effect in crystals.

The most important assumption involved is the assumption of perfect rather than approximate commutation. Valid questions are: How much error does the assumption of perfect Bose commutation introduce? What is the precise definition of the low excitation region? Similar assumptions have been used in the theory of

superconductivity (7), and they are a common starting point in theoretical treatments of ferromagnetism and the spin wave formalism (12, 13). They appear to be adequate in these cases even when a perturbation treatment fails.

Comparison with Perturbation Theory

In the exciton problem a comparison of results derived by perturbation theory and by second quantization is possible, although difficult. Agranovich's solution includes interactions of the ground state with states that are doubly excited, quadruply excited, etc., and of single excitons with triple excitons, etc.; all these contributions enter in higher orders of the perturbation theory. Thus it is clear that the

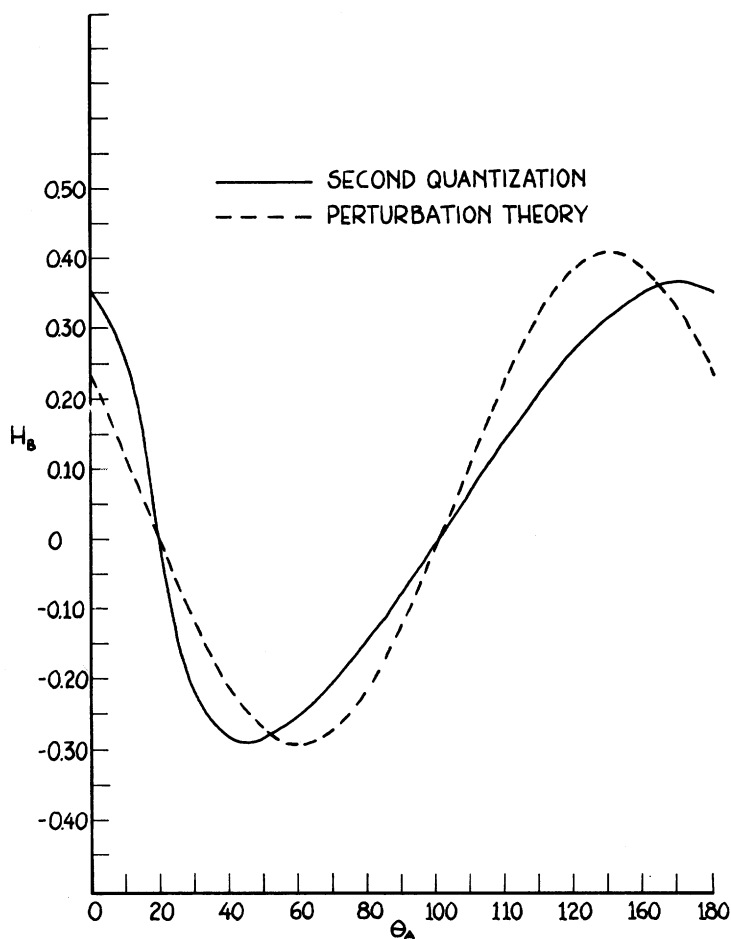


FIG. 1. Hypochromism (H_B) in a linear chain as a function of θ_A (in degrees) for $\theta_B = \theta_A + \pi/3$, $f_A = 1.0 = f_B$, $E_A = 6.20$ eV, $E_B = 4.77$ eV, $R_0 = 6\text{\AA}$.

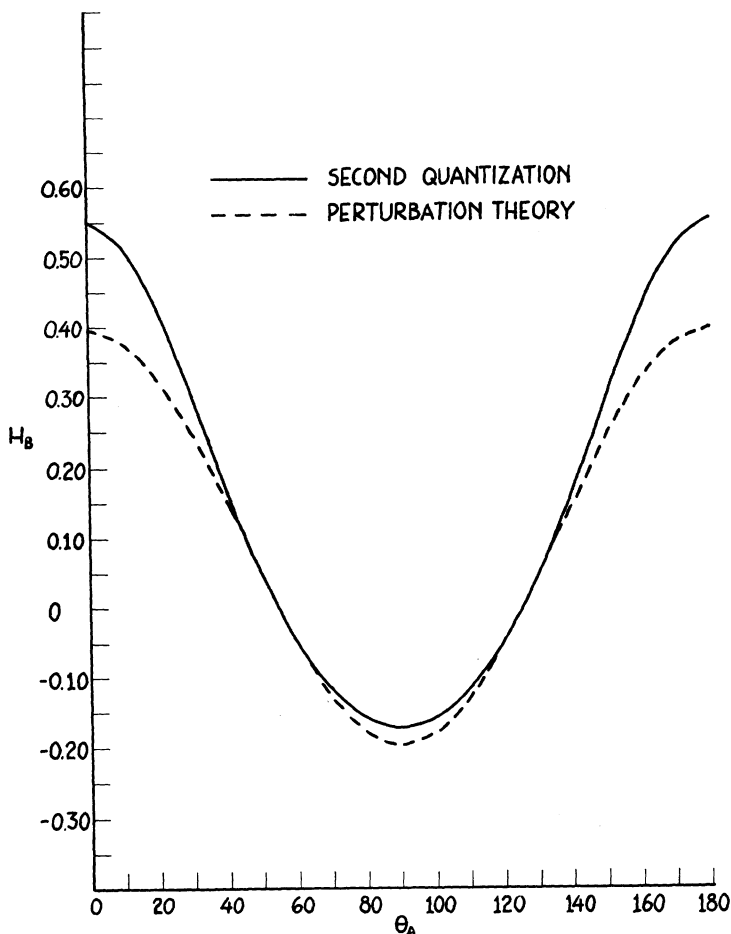


FIG. 2. Hypochromism (H_B) in a linear chain as a function of θ_A (in degrees) for $\theta_B = \theta_A$, $f_A = 1.00$, $f_B = 0.01$, $E_A = 6.20$ ev, $E_B = 4.77$ ev, $R_0 = 8$ A.

second quantized treatment brings in contributions from all orders of perturbation theory, but we are ignorant as to how much of each order contribution is included. Unfortunately here the picture has been confused by two erroneous calculations which reported considerable disagreement between results of the two theories. Agranovich (5) attempted an *a posteriori* perturbation expansion of his results in order to compare his calculations with those of Craig (14). In deriving the changes in wave functions, a relation between the Bose amplitudes U and V (equation 5 of reference 5) was used improperly for the case of a single excitation only. For the latter, $V = 0$, and Agranovich's equation 9 and the section comparing with Craig's results are wrong. The comparison is invalidated, and as a matter of fact we have

been able to show, at least for the case of one molecule in a unit cell, that such an *a posteriori* expansion of the second quantized results agrees to first order in the perturbation theory.

The second erroneous conclusion was made by us (15) in comparing with a calculation on hypochromism in polynucleotides made by Tinoco (16). Here the formulas of Agranovich were corrected, but a numerical mistake, as well as one of interpretation, led to apparent disagreement.

Feeling the need for an accurate comparison, we have carried out from scratch calculations by both methods on as simple a system as possible—an infinite linear chain of identical three-level units.³ The details of the calculation are presented in the Appendix. The results show, in general, good agreement between second quantized and perturbation theory quantities. An illustration of the agreement is given in Figs. 1 and 2, where we plot for both cases the calculated hypochromism, i.e., the change in oscillator strength of the lower transition on going from monomer to polymer. The cases chosen for illustration are strongly coupled, and the discrepancy between the two curves is maximized. For weaker coupling the curves nearly coincide. It is satisfying that the two approximations agree as well as they do; we feel that the differences are minor although not insignificant. We must, however, express pessimism regarding recourse to experiment to decide which approach is really better; naturally occurring systems are hardly as simple as a three-level model.

III. CONCLUSIONS

We have outlined Agranovich's solution of the molecular exciton problem in which the representation of second quantization is used. The assumptions of the theory, in particular the manipulation of excitons as bosons, have been stressed. This technique allows a closed solution without the use of a perturbation expansion and formally simplifies the consideration of interactions with photons or phonons. Previous calculations implying major disagreement between second quantized results and those obtained by first-order perturbation theory are incorrect. A detailed comparison of the two theories for a perfect one-dimensional aggregate shows in general good agreement. Thus the use of either formalism is valid, the choice dictated by convenience of one or the other in the particular problem studied.

APPENDIX

Consider an infinite aggregate of identical molecules, with complete translational symmetry in one dimension. Let each molecule possess a ground state 0 , a first excited state B , and a second excited state A . Let the transition dipoles to these molecular states lie in a plane, making angles A and B with the axis of the polymer.

³ The method of Agranovich in principle cannot be used for small aggregates such as dimers and trimers, where N is small. In practice it gives results also in agreement with perturbation theory to first order.

Further, let the separation of the point dipoles be R_0 , and let the corresponding transition oscillator strengths, f_A and f_B , be given. The input parameters for the problem are then E_A, E_B, f_A, f_B , angles A, B , and R_0 . In atomic units, the magnitude of the transition moments may be obtained from the equations

$$f_K = \frac{2}{3} |\mu_K|^2 E_K$$

The following lattice sums enter the problem

$$G_{AA} = 2G |\mu_A|^2 R_0^{-3} (1 - 3 \cos^2 A)$$

$$G_{BB} = 2G |\mu_B|^2 R_0^{-3} (1 - 3 \cos^2 B)$$

$$G_{AB} = 2G |\mu_A| |\mu_B| R_0^{-3} [\cos(A - B) - 3 \cos A \cos B] = G_{BA}$$

where

$$G = \sum_{L=1}^{\infty} \frac{1}{L^3} = 1.2020569 \dots$$

First-order perturbation theory gives for the $K = 0$ level of the exciton band (the only one to which a transition is dipole-allowed)

$$E_{A'} = E_A + G_{AA} \quad \frac{f_{A'}}{N f_A} = 1 - \frac{4 \cos(A - B) (E_A E_B)^{1/2} G_{AB}}{E_B^2 - E_A^2} \left(\frac{f_B}{f_A} \right)^{1/2}$$

with a similar expression for B with A and B interchanged.⁴

In Agranovich's method one first defines

$$\epsilon_A = (E_A^2 + 2G_{AA}E_A)^{1/2} \quad \epsilon_B = (E_B^2 + 2G_{BB}E_B)^{1/2}$$

$$\gamma_{AB} = (E_A E_B / \epsilon_A \epsilon_B)^{1/2} G_{AB}$$

The following set of equations must be solved

$$(E - \epsilon_A)U_A - 2\gamma_{AB}\epsilon_B(E + \epsilon_B)^{-1}U_B = 0$$

$$-2\gamma_{AB}\epsilon_A(E + \epsilon_A)^{-1}U_A + (E - \epsilon_B)U_B = 0$$

subject to the normalization condition

$$U_A^2 \epsilon_A (E + \epsilon_A)^{-2} + U_B^2 \epsilon_B (E + \epsilon_B)^{-2} = (4E)^{-1}$$

The energies are given by (A corresponding to $+$, B to $-$)

$$E_{\pm}^2 = \frac{1}{2}(\epsilon_A^2 + \epsilon_B^2) \pm \frac{1}{2}[(\epsilon_A^2 - \epsilon_B^2)^2 + 16\epsilon_A\epsilon_B\gamma_{AB}^2]^{1/2}$$

and the chromic effect for A by

⁴ First given by D. L. Dexter (16) and independently by I. Tinoco (17) and W. Rhodes (18).

$$\frac{f'_A}{Nf_A} = \frac{f_+}{Nf_A} = \frac{4E_+\epsilon_A U_{A+}^2}{(E_+ + \epsilon_A)^2} + \frac{4E_+\epsilon_B U_{B+}^2 + f_B}{(E_+ + \epsilon_B)^2 f_A} + \frac{6f_B^{1/2} E_+ U_{A+} + U_{B+} (\epsilon_A \epsilon_B)^{1/2} \cos(A - B)}{f_A^{1/2} (E_+ + \epsilon_A) (E_+ + \epsilon_B)}$$

with a similar expression valid for B , but with $+$ and $-$, and A and B , interchanged. The sum rule, though not obvious, may be proved.

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