

Cooperative Jahn-Teller phase transition of icosahedral molecular units

Seyed H. Nasrollahi and Dimitri Vvedensky

The Blackett Laboratory, Imperial College London, London SW7 2AZ, United Kingdom

Abstract.

Non-linear molecules undergo distortions when the orbital degeneracy of the highest occupied level is lifted by the Jahn-Teller effect. If such molecules or clusters of atoms are coupled to one another, the system may experience a cooperative Jahn-Teller effect (CJTE). In this paper, we describe a model of how the CJTE leads to the crystallization of the disordered phase. The model Hamiltonian is based on a normal mode decomposition of the clusters in order to maintain the symmetry labels. We take account of the electron-strain and the electron-phonon couplings and, by displacing the coordinates of the oscillators, obtain a term that explicitly couples the Jahn-Teller centers, enabling us to perform a mean-field analysis. The calculation of the free energy then becomes straightforward, and obtaining phase diagrams in various regimes follows from the minimization of this free energy. The results show that the character of the phase transition may change from strong to weak first order and even to second-order, depending on the coupling to the vibrational modes. Taken together, these results may serve as a paradigm for crystallization near the transition temperature, where the atoms tend to form clusters of icosahedral symmetry.

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1. Introduction

The Jahn-Teller theorem states that a non-linear molecule that has electronic degeneracy at the highest occupied molecular orbital (HOMO) is unstable and will distort to remove the degeneracy. This effect originates with the interactions between electrons and atomic vibrations, called vibronic interactions, resulting in a lowering of the symmetry of the molecule to reduce the degeneracy of the highest occupied states.

In the Taylor expansion of the molecular potential energy about equilibrium, the higher-order terms determine the vibronic interaction operator [?, ?]. In the adiabatic approximation, the off-diagonal terms are set to zero and the vibronic interaction can be treated as a perturbation, with the correction to the energy obtained by using degenerate perturbation theory. This distorts the adiabatic potential energy surface (APES), causing minima to be at points other than the equilibrium configuration. Hence, the molecule is unstable at the equilibrium point and will distort to minimize its potential energy. This is called the Jahn-Teller effect (JTE) [?].

In a collection of coupled Jahn-Teller centers, the distortions are aligned below some transition temperature. In a crystal, this effect would lower the symmetry of the lattice. This is called the cooperative Jahn-Teller effect (CJTE). Dunitz and Orget [?] and McClure [?] were the first to propose the possibility of a cooperative Jahn-Teller phenomenon. Wojtowicz [?] and Kanamori [?] were among the first to establish a theory of the CJTE, with later work by Elliott *et al.* [?, ?, ?], Englman and Halperin [?], Pytte [?], Kino *et al.* [?], completing the picture.

Early work in this area was concerned largely with doubly- or triply-degenerate orbitals that were coupled to single or doubly-degenerate normal modes. This enabled the analytic determination of physical quantities, such as the free energy, the transition temperature, and the strain [?]. The computational complexity increases for greater numbers of degenerate electronic states, with the Jahn-Teller effect of a molecule with icosahedral symmetry being one of the most computationally challenging scenarios because there can be three- four-, or five-fold degenerate electronic states that can be coupled to four- and five-fold degenerate modes.

The static Jahn-Teller effect for icosahedral molecules was first discussed by Khlopin *et al.*, [?] and later by Pooler [?], who emphasized the symmetry and group theoretical aspects of such systems. Ceulemans and Fowler [?] and Cullerne *et al.*, [?, ?] were concerned with the potential energy surface and Ham reduction factors of the static $G \otimes (g \oplus h)$ problem, where four-fold degenerate electronic states (G) couple with four- and five-fold degenerate vibrational states (g) and (h),

respectively. Dunn *et al.*, [?, ?] and O'Brien [?] focussed on the potential energy surface and the corresponding minima of the static $T \otimes h$ problem, in which three-fold degenerate electronic states (T) couple with five-fold degenerate vibrational states (h).

In this paper, we investigate the most complex of the cooperative Jahn-Teller systems, those involving interacting icosahedral clusters, the $H \otimes (g \oplus 2h)$ CJTE. The static $H \otimes (g \oplus 2h)$ problem was first investigated with the calculation of the APES extremal points by Ceulemans and Fowler [?], with additional work by Rios *et al.* [?] and Moate *et al.*, [?] Despite this work, little attention has been devoted to the cooperative effect of icosahedral molecules. Dunn [?] and Moujaes and Dunn *et al.*, [?] were among the few who examined the CJTE of icosahedral clusters. However, unlike the present work, their main concern was the CJTE due to triply-degenerate orbitals. This effect is exhibited by the excited states of C_{60} and its anions because the lowest unoccupied molecular orbital (LUMO) of C_{60} is three-fold degenerate. [?]

The $H \otimes (g \oplus 2h)$ CJTE is concerned with five-fold degenerate electronic states (H). From group theory [?, ?], these states can be vibronically coupled to the A_{1g} , G_g and $2H_g$ normal modes. The A_{1g} is the fully symmetric normal mode and, hence, does not correspond to any distortions of the symmetry. The complication arises because of the double appearance of H_g in the decomposition. This does not necessarily imply that there are couplings to two different vibrational modes of H_g symmetry [?], but the Wigner-Eckart theorem does not take its usual form [?] and there are two different ways to couple to a vibrational mode, and hence two independent sets of Clebsch-Gordan coefficients are needed. This means that we need two coupling constants and two matrices to separate the matrix elements into reduced elements and coefficients [?]. The choice of the Clebsch-Gordan coefficients in this case is free as long as any pair of linear combinations of the two will do equally well [?]. This is effectively the same as the coupling to two H_g modes, but the complication can be partially alleviated by a multi-mode analysis, which reduces the number of coupled coordinates from fourteen to nine.

Determining the free energy of this system necessitates finding the eigenvalues of a five-dimensional matrix composed of nine coordinates and three coupling constants. Equations for the distortions in each coordinate are obtained by minimizing the free energy with respect to all nine coordinates and solving the resulting equations simultaneously at a variable temperature.

Phase diagrams are determined by minimizing the free energy for specific thermodynamic conditions. There are two main factors that affect the phase diagrams. One is the minimum of the potential

surface. Essentially the Jahn-Teller effect warps the nine-dimensional APES into one with several potential minima instead of only one. Hence, we can have as many phase diagrams as there are minima of the APES, each corresponding to a particular distortion of the icosahedral clusters. The second factor is the absolute and relative values of the three coupling constants of the electronic states to the vibrational modes. These can affect the character of the phase diagrams as well as the transition temperatures. More specifically, for the D_{5d} minima of the APES, the transition changes from strongly first order to second order, depending on the parameter that represents the coupling to the H_g modes.

The HOMO of C_{60} is five-fold degenerate [?], so a system of interacting cations of C_{60} may undergo such a transition. Si_{12} is another example of a cluster that can experience such a JTE [?]. The $H \otimes (g \oplus 2h)$ CJTE may also be relevant to the metallic glasses near the glass transition temperature [?], where the atoms tend to form clusters of icosahedral symmetry. This will be discussed in more details in the conclusions.

The organization of our paper is as follows. In Sec. ?? we describe the basic formalism we use, including the passage from the single cluster to the coupled-cluster Hamiltonian, and the application of mean-field theory to the free energy obtained from the partition function. Our formulation is general and can be applied to a coupled Jahn-Teller system with any symmetry. Section ?? applies the formulation in Sec. ?? to icosahedral clusters, focussing on the application of symmetry principles to the formulation of the free energy and the computation of phase diagrams for coupled Jahn-Teller systems. Phase diagrams are presented in Sec. ?? in increasing order of complexity. We discuss how the various couplings affect the transition temperature, the order of the transition, and other aspects of the phase diagram. Section ?? summarizes our work and provides an outlook to other applications of our formulation. Details of the calculations in the following sections, including figures of the vibrational normal modes, may be found in [?].

2. Basic Formulation

2.1. Single-Cluster Hamiltonian

The vibronic operator contains the molecular coordinates in a power series, though, for simplicity, we will work only up to the linear term. Normal coordinates are convenient for Jahn-Teller problems, with each such coordinate corresponding to an irreducible representation of the symmetry group of the molecule. The vibronic operator up to the linear order is the JT part

of the total Hamiltonian:

$$H_{JT} = \sum_{\Gamma\gamma} F_{\Gamma} Q_{\Gamma\gamma} \hat{O}_{\Gamma\gamma}. \quad (1)$$

Here, F_{Γ} are the coupling coefficients, $Q_{\Gamma\gamma}$ the normal coordinates and $\hat{O}_{\Gamma\gamma}$ the corresponding matrices. Including the kinetic and potential energies of the normal modes yields the total Hamiltonian of the molecule:

$$H = \sum_{\Gamma\gamma} \left(\frac{P_{\Gamma\gamma}^2}{2M} + \frac{1}{2} M \omega_{\Gamma}^2 Q_{\Gamma\gamma}^2 + F_{\Gamma} Q_{\Gamma\gamma} \hat{O}_{\Gamma\gamma} \right), \quad (2)$$

where M is the effective mass, $P_{\Gamma\gamma}$ the momentum, and ω_{Γ} the natural frequency of the normal modes.

2.2. Coupled-cluster Hamiltonian

The passage from a single Jahn-Teller center to the CJTE is obtained by summing the single-molecule Hamiltonians and adding an intermolecular interaction term. There are several ways to couple the vibrations to the orbitals in a system of interacting JT centers. Although the $\mathbf{k} = 0$ limit of the acoustic phonon modes leads to macroscopic strain, treating them separately is useful due to the problem of applying proper boundary conditions to the strained crystal [?]. Kanamori [?] was primarily concerned with the coupling to the elastic strain because his calculations were in the limit $\mathbf{k} = \mathbf{0}$, where the acoustic phonons are simple translations and, hence, do not couple to the orbitals. Pytte [?] used a similar model, assuming that the dominant coupling is to the strains. Englman and Halperin [?] and Feiner [?] coupled the coordinates of the JT centers directly, whereas Elliott [?] considered the coupling to optical phonon modes at $\mathbf{k} = \mathbf{0}$, although elastic strains were taken into account as well.

After considering the lattice-orbit coupling in a system of interacting JT centers, the centers must be coupled to each other. Gehring and Gehring [?] discuss four mechanisms for this interaction. (i) Perturbation theory, where the ions are coupled through the vibronic matrices [?]. (ii) Displaced oscillators, based on a transformation of the phonon creation and annihilation operators [?]. This results in essentially the same interaction term as perturbation theory, and is the method used here. (iii) Factorization of the partition function, which does not seem very promising. (iv) Canonical transformations, which are similar to displaced operators.

Here, we take a somewhat different approach. We begin with the assumption that the inter-cluster interactions are weaker than the intra-cluster interactions. Hence, we absorb the ion-ion interactions into the strain energy and allow the clusters to maintain their normal modes. In addition, we couple

the uniform strains to the electrons. This leads to the Hamiltonian:

$$H = \sum_{\mathbf{R}\Gamma\gamma} \left[\frac{1}{2} \Omega \eta_{\Gamma} e_{\Gamma\gamma}^2 + \frac{P_{\Gamma\gamma}^2(\mathbf{R})}{2M} + \frac{1}{2} M \omega_{\Gamma}^2 Q_{\Gamma\gamma}^2(\mathbf{R}) + V_{\Gamma} e_{\Gamma\gamma} \widehat{O}_{\Gamma\gamma}(\mathbf{R}) + F_{\Gamma} Q_{\Gamma\gamma}(\mathbf{R}) \widehat{O}_{\Gamma\gamma}(\mathbf{R}) \right], \quad (3)$$

where \mathbf{R} is the mean position of the center of the atomic clusters, and Ω , η_{Γ} , V_{Γ} and e are the volume, elastic constant, electron-strain coupling constant, and the strain, respectively.

Although ours is an approximate approach, we are able to maintain the symmetry representations of the JT distortion of the clusters. We are also able to transform into displaced coordinates while maintaining the same operator commutation relations. If more than one type of normal coordinate is coupled to the orbitals, the displaced coordinates will not satisfy the commutation relations. However, in our approach, instead of relating the normal coordinates of the clusters to the phonons in an approximate way,

$$Q_{\Gamma\gamma} \approx \sqrt{\frac{\hbar}{2M\omega_{\Gamma}}} (a^{\dagger}(\mathbf{k}) + a(\mathbf{k})), \quad (4)$$

we define the ladder operators in terms of the symmetries of the normal coordinates, leaving no ambiguity in relating the two. This allows us to transform the operators even if there are vibronically coupled normal coordinates of different symmetries. The only cost is that the inter-cluster interaction appears only after determining the values of the strains and transformation of the ladder operators.

We proceed by substituting the uniform strain with the value obtained from the minimization of the Hamiltonian. We also write the coordinates, conjugate momenta and the matrices as Fourier series and define ladder operators in the usual way and substitute into the Hamiltonian. Transforming the operators into displaced coordinates makes the Hamiltonian free of any linear terms in matrices.

Finally, transforming the matrices back to spatial coordinates produces,

$$H = H_0 + \sum_{\Gamma,\gamma} \left\{ \sum_{\mathbf{k}} \left[\hbar \omega_{\Gamma}(\mathbf{k}) \left(\gamma_{\Gamma\gamma}^{\dagger}(\mathbf{k}) \gamma_{\Gamma\gamma}(\mathbf{k}) + \frac{1}{2} \right) \right] - \frac{1}{2} \sum_{\mathbf{R}' \neq \mathbf{R}} \left[J_{\Gamma}(\mathbf{R}, \mathbf{R}') + \frac{V_{\Gamma}^2}{\Omega \eta_{\Gamma}} \right] \widehat{O}_{\Gamma\gamma}(\mathbf{R}) \widehat{O}_{\Gamma\gamma}(\mathbf{R}') \right\}, \quad (5)$$

where

$$J_{\Gamma}(\mathbf{R}, \mathbf{R}') = \frac{1}{N} \sum_{\mathbf{k}} \frac{2(\xi_{\mathbf{k}}^{\Gamma})^2}{\hbar \omega_{\Gamma}(\mathbf{k})} e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')}. \quad (6)$$

The explicit derivation of this CJTE Hamiltonian is shown in Appendix A. Note that the term for $\mathbf{R} = \mathbf{R}'$ is the self-energy and can be included in H_0 , along with

other non-dynamical terms, such as the crystal energy. The terms with $\mathbf{R} \neq \mathbf{R}'$ represent the interaction between local distortions at \mathbf{R} and \mathbf{R}' mediated by the JT effect which drive the phase transition [?].

3. Mean-field approximation

We have made two approximations. First, we included only the linear term of the vibronic operator and neglected the higher-order terms. Although the second-order terms can be important, they are difficult to compute for complex systems. Second, we assumed that the intra-cluster are stronger than the inter-cluster interactions, so that the clusters will maintain their normal modes and the inter-cluster interactions were considered to be part of the uniform strain energy. However, this should not be a problem because the way that the ladder operators and their transformation to displaced coordinates were defined, made the inter-cluster interaction explicit at the end. Hence, we are able to perform a mean-field approximation at this stage, which is the third approximation.

The general idea of the mean-field approximation is to reduce the many-body problem to a single-body problem by assuming that each unit cell is affected only by the average of the fields from all other cells. This average field will play the role of the order parameter which vanishes in the high-temperature phase. In the case of the CJTE, the mean-field is the average order of the local distorted clusters or, in other words, the extent to which the distorted clusters are aligned with each other.

In our Hamiltonian (??), the last term is an indication of a coupling between the operators $\widehat{O}_{\Gamma\gamma}(\mathbf{R})$. We allow the matrices to fluctuate around their thermal average values:

$$\widehat{O}_{\Gamma\gamma}(\mathbf{R}) = \langle \widehat{O}_{\Gamma\gamma} \rangle + \Delta \widehat{O}_{\Gamma\gamma}(\mathbf{R}), \quad (7)$$

where,

$$\langle \widehat{O}_{\Gamma\gamma} \rangle = \frac{1}{\mathcal{Z}} \text{Tr}(\widehat{O}_{\Gamma\gamma} e^{-\beta \widehat{H}}), \quad (8)$$

and \mathcal{Z} is the partition function and $\beta = (k_B T)^{-1}$, where k_B is Boltzmann's constant and T is the absolute temperature. The mean-field correlation term is,

$$\begin{aligned} & - \frac{1}{2} \sum_{\mathbf{R}' \neq \mathbf{R}} \widehat{O}_{\Gamma\gamma}(\mathbf{R}) \widehat{O}_{\Gamma\gamma}(\mathbf{R}') \\ &= - \frac{1}{2} \sum_{\mathbf{R}' \neq \mathbf{R}} [(\langle \widehat{O}_{\Gamma\gamma} \rangle + \Delta \widehat{O}_{\Gamma\gamma}(\mathbf{R}))][(\langle \widehat{O}_{\Gamma\gamma} \rangle + \Delta \widehat{O}_{\Gamma\gamma}(\mathbf{R}'))] \\ &= - \frac{1}{2} \langle \widehat{O}_{\Gamma\gamma} \rangle^2 - \sum_{\mathbf{R}} \langle \widehat{O}_{\Gamma\gamma} \rangle \Delta \widehat{O}_{\Gamma\gamma}(\mathbf{R}) + O(\Delta \widehat{O}_{\Gamma\gamma})^2 \\ &= \frac{1}{2} \langle \widehat{O}_{\Gamma\gamma} \rangle^2 - \sum_{\mathbf{R}} \langle \widehat{O}_{\Gamma\gamma} \rangle \widehat{O}_{\Gamma\gamma}(\mathbf{R}) + O(\Delta \widehat{O}_{\Gamma\gamma})^2. \end{aligned} \quad (9)$$

In the last equality we substituted equation (??) into the second term. The resulting Hamiltonian consists of a second-order term in the average fields, a term linear in the matrices and a second-order term in thermal fluctuations which will be ignored in the spirit of the mean-field approximation.

The glory of this approximation is that we do not need to calculate every single pair interaction, but instead we only need to calculate the potential of a single site affected by the average field from all other sites. Note that we are not trying to calculate the correlation function $\sum \langle \hat{O}_{\Gamma\gamma}(\mathbf{R}) \hat{O}_{\Gamma\gamma}(\mathbf{R}') \rangle$ which measures how microscopic variables are related and covary with each other across space, but we are merely simplifying part of the Hamiltonian (??) using mean-field approximation.

The thermal averages are taken to be site-independent because we are assuming that the system is invariant under translations. This assumption will not be valid if the system is not homogeneous throughout the space, or in other words, the symmetry of the system is lower than that of the Hamiltonian [?]. Since we are mainly concerned with the CJTE in crystalline structures and isotropic supercooled liquid phases, this assumption is perfectly valid.

In general, mean-field approximation is more accurate for longer range of interactions, smaller fluctuations and higher dimensions where the coordination number is higher [?]. In fact, the theory becomes exact for infinite interaction range and number of nearest neighbors [?]. As can be seen from equation (??), the electron-strain coupling radius is infinite. Moreover the atoms interact in a three-dimensional environment with an average coordination number of twelve for icosahedral clusters. Hence for high contribution of electron-strain coupling to the inter-cluster interaction and a strong vibronic coupling (where the correlation length is longer than the lattice constant), the mean-field approach can be quite reliable. Nevertheless, mean-field theory can still give a reasonable qualitative picture of the problem. A good quantitative measure of the validity of the theory is the Ginzburg criterion which considers the theory to be valid as long as the correlation between thermal fluctuations over a coherence volume is much less than the order parameter itself, i.e., $\langle (\Delta \hat{O}_{\Gamma\gamma}^2)_{coh} \rangle \ll \langle \hat{O}_{\Gamma\gamma}^2 \rangle$ [?]. The systematic calculation of the correlation function is quite challenging because we are dealing with a three-dimensional quantum system with large non-commutative matrix operators. However, for the reasons noted above, we expect agreement with the mean-field result for the first-order transitions.

Proceeding with the theory, H_0 and the phonon energy term (the operators $\gamma_{\Gamma\gamma}(\mathbf{k})$ have zero averages [?]) only add a non-dynamical constant term to the free

energy which do not affect the phase diagrams and thus we ignore them from this point onwards. The mean-field Hamiltonian is

$$H = \sum_{\Gamma\gamma} \left[\frac{1}{2} \lambda_{\Gamma} \langle \hat{O}_{\Gamma\gamma} \rangle^2 - \sum_{\mathbf{R}} \lambda_{\Gamma} \langle \hat{O}_{\Gamma\gamma} \rangle \hat{O}_{\Gamma\gamma}(\mathbf{R}) \right], \quad (10)$$

where,

$$\lambda_{\Gamma} = \sum_{\mathbf{R}' \neq \mathbf{R}} J_{\Gamma}(\mathbf{R}, \mathbf{R}') + \frac{V_{\Gamma}^2}{\Omega \eta_{\Gamma}}, \quad (11)$$

and λ_{Γ} is site-independent because we are treating all units as the same. Thus, no matter what site \mathbf{R} is chosen, $\sum_{\mathbf{R}' \neq \mathbf{R}} J_{\Gamma}(\mathbf{R}, \mathbf{R}')$ will always return the same value.

The partition function \mathcal{Z} is calculated from from the Hamiltonian (??) as

$$\mathcal{Z} = \text{Tr} \left(e^{-\beta \hat{H}} \right) = \exp \left(-\frac{\beta}{2} \sum_{\Gamma\gamma} \lambda_{\Gamma} \langle \hat{O}_{\Gamma\gamma} \rangle^2 \right) \sum_i e^{\beta w_i}, \quad (12)$$

in which the w_i are the eigenvalues of

$$\sum_{\mathbf{R}, \Gamma, \gamma} \lambda_{\Gamma} \langle \hat{O}_{\Gamma\gamma} \rangle \hat{O}_{\Gamma\gamma}(\mathbf{R}). \quad (13)$$

The mean-field approximation to the free energy F of a system of interacting JT centers is then given by

$$F = -\frac{N}{\beta} \ln \mathcal{Z} = \sum_{\Gamma, \gamma} \frac{N}{2} \lambda_{\Gamma} \langle \hat{O}_{\Gamma\gamma} \rangle^2 - \frac{N}{\beta} \ln \sum_i e^{\beta w_i}. \quad (14)$$

The stable phase in systems at constant pressure and temperature is that which has a lower Gibbs free energy. However, we may only derive the Helmholtz free energy (which requires the system to be at constant volume and temperature), not the Gibbs free energy, from the statistical partition function through equation (??) [?]. Nonetheless, since we are mainly concerned with condensed phases of matter that undergo CJTE (mainly solids, but could be liquid as well), the volume and pressure changes in such transitions are of negligible amount. Thus we may assume that the two thermodynamic potentials are approximately equal and use them interchangeably [?, ?].

4. Icosahedral Clusters

The symmetry group of an icosahedral molecule is I_h . We are concerned here with the electronic d -orbitals, which are not split by the icosahedral crystal field. Hence, these states all transform according to the five-fold degenerate representation H_g of I_h .

According to the matrix element method, only the vibrational modes that transform according to A_g , G_g and H_g representations are coupled to the d -orbitals. For notational simplicity, we will henceforth omit the subscript g for irreducible representations, as odd representations are not involved in the interactions.

As discussed in the introduction, there is the complication of the multiplicity of the representation H in the decomposition $[H \otimes H] = A + G + 2H$. This means that the coupling to the five-fold degenerate vibrational mode ($H \otimes h$) involves a sum of interaction matrices with two coupling constants because the Wigner–Eckart theorem does not take its usual form. Thus, to represent a general JT interaction, two families of matrices must be multiplied by independent coupling constants [?]. We are free to choose these matrices insofar as any linear combination will do equally well.

Neglecting the totally symmetric normal mode, which does not result in a distortion, there are 9 modes coupled to the d -orbitals in an icosahedral molecule. We denote the five-fold symmetric normal modes by h and the four-fold modes by g .

4.1. The free energy

We decompose the vibronic matrices into a sum of the operators for each normal mode so we can make use of the mean-field Hamiltonian (??). The most general form of the *mean-field* operator of vibronic interactions that couples the five-fold degenerate electronic orbitals to the 9 normal modes of vibration is,

$$W = \sum_{\mathbf{R}, \gamma} \left\{ \lambda_g \langle \widehat{O}_{g\gamma} \rangle \widehat{O}_{g\gamma}(\mathbf{R}) + \lambda_h [\langle \widehat{O}_{h\gamma}^a \rangle \widehat{O}_{h\gamma}^a(\mathbf{R}) \sin \alpha + \langle \widehat{O}_{h\gamma}^b \rangle \widehat{O}_{h\gamma}^b(\mathbf{R}) \cos \alpha] \right\}, \quad (15)$$

where α can take values from 0 to 2π . With the following substitutions:

$$\begin{aligned} \lambda_g &= \lambda g^2, \\ \lambda_h \sin \alpha &= \lambda a^2, \\ \lambda_h \cos \alpha &= \lambda b^2, \end{aligned} \quad (16)$$

we may factor out the coupling strength λ and absorb the numbers g , a and b into the matrices (we may take the negative root of these numbers depending on α). The mean-field vibronic matrix becomes,

$$W = \sum_{\mathbf{R}, \gamma} \lambda \left[\langle \widehat{O}_{g\gamma} \rangle \widehat{O}_{g\gamma}(\mathbf{R}) + \langle \widehat{O}_{h\gamma} \rangle \widehat{O}_{h\gamma}(\mathbf{R}) \right], \quad (17)$$

and the corresponding free energy is:

$$F = \sum_{\Gamma, \gamma} \frac{N}{2} \left(\lambda \langle \widehat{O}_{g\gamma} \rangle^2 + \langle \widehat{O}_{h\gamma} \rangle^2 \right) - \frac{N}{\beta} \ln \sum_i e^{\beta w'_i} \quad (18)$$

where w'_i are the eigenvalues of (??).

We may write the free energy as a dimensionless density with a reduced temperature with the following substitutions:

$$f = \frac{F}{N\lambda}, \quad t = \frac{1}{\beta\lambda}, \quad w_i = \frac{w'_i}{\lambda}. \quad (19)$$

Note that λ has dimensions of energy. Therefore, the dimensionless free energy density is,

$$f = \sum_{\gamma} \frac{1}{2} \left(\langle \widehat{O}_{g\gamma} \rangle^2 + \langle \widehat{O}_{h\gamma} \rangle^2 \right) - t \ln \sum_i e^{w_i/t} \quad (20)$$

4.2. Coordinates and electronic parameters

The method of Öpik and Pryce [?] enables us to find the coordinates of the extrema of the adiabatic potential without diagonalizing the vibronic matrix to find its eigenvalues. We use this method to write the JT-induced coordinates in terms of five electronic parameters. Hence, the extremal points are determined in a space of 5 dimensions instead of 9. This method simplifies the determination of the coordinates of the potential minima, but not the eigenvalues of the vibronic matrix. The calculation has been done by Ceulemans and Fowler [?] and is shown in appendix B.

We use these coordinates to simplify the minimization of the free energy and the determination of phase diagrams. The coordinates of some extremal points of the potential surface are calculated from the five-dimensional coordinates (taken from [?]) and listed in Table ???. These points can be either local minimum or maximum, depending on the JT stabilization energies. These energies depend on the vibronic coupling constants and the vibrational frequencies of the normal. The explicit expressions for JT energies of a single icosahedral molecule can be found in [?].

5. Phase Diagrams of cooperative Jahn-Teller phase transitions

The phase diagrams may be obtained by simultaneously minimizing the dimensionless free energy density (??) with respect to the average distortions $\langle \widehat{O}_{\Gamma\gamma} \rangle$:

$$\frac{\partial f}{\partial \langle \widehat{O}_{\Gamma\gamma} \rangle} = 0, \quad (21)$$

for all $\langle \widehat{O}_{\Gamma\gamma} \rangle \neq 0$.

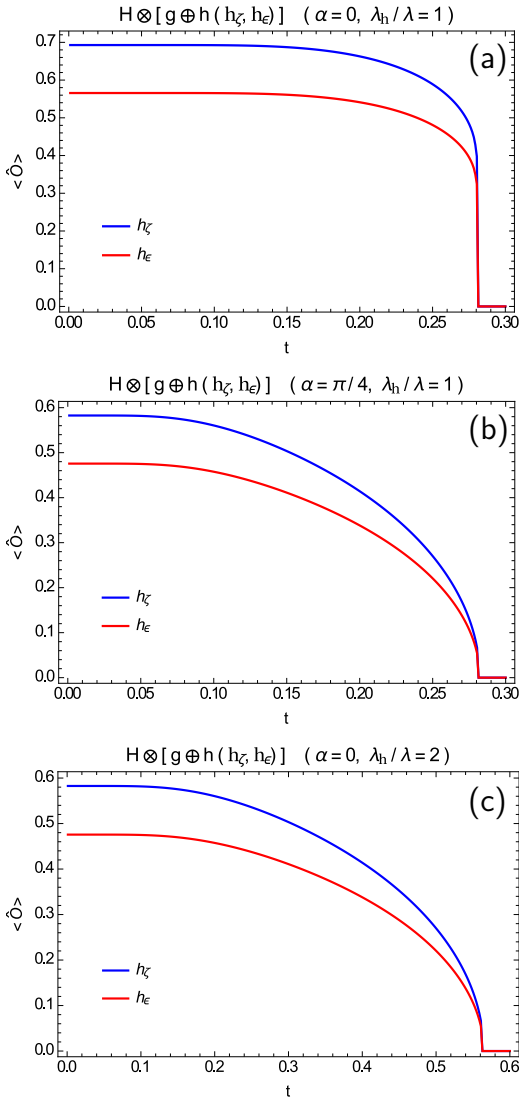
In calculating phase diagrams, we use the matrices of Ceulemans and Fowler [?], where we replace the coupling constants F_g , F_{Ha} and F_{Hb} by g , a and b . The calculations are based on the minimization of the dimensionless free energy density (??) using *Mathematica* [?].

5.1. $H \otimes [g + h(\mathbf{h}_\epsilon, \mathbf{h}_\zeta)]$

The simplest cooperative Jahn-Teller system distorts only the coordinates h_ϵ and h_ζ . The solutions are the values of the order parameters $\langle \widehat{O}_{h\epsilon} \rangle$ and $\langle \widehat{O}_{h\zeta} \rangle$ in terms of the reduced temperature t . These have been solved

Table 1. The extrema of the APES of an icosahedral $H \otimes (g + h)$ Jahn-Teller system. Only the top three extrema are used in our analysis.

Symmetry	$(\theta, \epsilon, \xi, \eta, \zeta)$	g_a	g_x	g_y	g_z	h_θ	h_ϵ	h_ξ	h_η	h_ζ
D_{5d}	$\frac{1}{\sqrt{5}}(0, \sqrt{2}, 0, 0, \pm\sqrt{3})$	0	0	0	0	0	$\frac{2\sqrt{2}}{5}b$	0	0	$\pm\frac{2\sqrt{3}}{5}b$
D_{5d}	$\frac{1}{\sqrt{10}}(\sqrt{3}, -1, 0, \pm\sqrt{6}, 0)$	0	0	0	0	$\frac{\sqrt{6}}{5}b$	$-\frac{\sqrt{2}}{5}b$	0	$\pm\frac{2\sqrt{3}}{5}b$	0
D_{3d}	$\frac{1}{\sqrt{3}}(\sqrt{2}, 0, 0, 0, \pm 1)$	$-\frac{\sqrt{6}}{9}g$	0	0	$\mp\frac{\sqrt{30}}{9}g$	$-\frac{2\sqrt{6}}{9}a$	0	0	0	$\mp\frac{2\sqrt{3}}{9}a$
D_{3d}	$\frac{1}{\sqrt{6}}(1, -\sqrt{3}, \pm\sqrt{2}, 0, 0)$	$-\frac{\sqrt{6}}{9}g$	$\pm\frac{3}{5}g$	0	0	$\frac{\sqrt{6}}{9}a$	$-\frac{\sqrt{2}}{3}a$	$\pm\frac{2\sqrt{3}}{9}a$	0	0
D_{3d}	$\frac{1}{\sqrt{3}}(0, 0, 1, 1, 1)$	$\frac{1}{\sqrt{6}}g$	$-\frac{3}{10}g$	$-\frac{3}{10}g$	$-\frac{\sqrt{30}}{18}g$	0	0	$\frac{2\sqrt{3}}{9}a$	$\frac{2\sqrt{3}}{9}a$	$\frac{2\sqrt{3}}{9}a$
	\vdots		\vdots		\vdots		\vdots		\vdots	

**Figure 1.** (Color online) Phase diagrams of a cooperative Jahn-Teller phase transition in coordinates h_ϵ and h_ζ of interacting icosahedral clusters. (a) $\alpha = 0, \lambda_h/\lambda = 1$, (b) $\alpha = \pi/4, \lambda_h/\lambda = 1$, and (c) $\alpha = \pi/4, \lambda_h/\lambda = 2$.

computationally for different values of α and λ_h/λ in equation (??) and the results are shown in Fig. ??.

Note that the values of $\langle \hat{O}_h \rangle$ at $t = 0$ match the values from Table ?? once we substitute for b from the relations (??). The factor α does not affect the critical temperature, but greatly affects the sharpness of the transition. When $\alpha = 0$, the transition is of the first kind, whereas for $\alpha = \pi/4$, it is a continuous second-order transition. In fact, the transition *continuously* changes from strongly first-order at $\alpha = 0$ to second-order at exactly $\alpha = \pi/4$. In the theory of the $H \otimes (g \oplus 2h)$ Jahn-Teller effect the $\alpha = \pi/4$ is special because the D_{5d} and D_{3d} minima of the APES become degenerate at this point and the D_{3d} minima becomes preferable above this value [?].

On the other hand, λ_h/λ only affects the critical temperature but not the overall shape of the phase diagram.

5.2. $H \otimes [g + h(h_\theta, h_\epsilon, h_\eta)]$

The next simplest cooperative Jahn-Teller phase transition is along the three coordinates h_θ, h_ϵ and h_η and the phase diagrams are shown in Fig. ?. Each additional distorted coordinate adds to the computational complexity of the problem where the vibronic matrix will have an additional non-zero variable entry and there is an additional simultaneous equation to solve. In fact, being a D_{5d} minimum of the APES, the behavior of this transition is similar to that discussed above, where it becomes second-order at $\alpha = \pi/4$.

5.3. $H \otimes [g(g_a, g_z) + h(h_\theta, h_\zeta)]$

In this phase transition, the d -orbitals are coupled to both the G_g and the H_g vibrational modes. This means we have an extra coupling coefficient g . What is important here is the ratio of the coupling strengths λ_g/λ_h , which tells us how strongly the modes are coupled to the orbitals. Three phase diagrams are shown in Fig. ?? for different values of g and α .

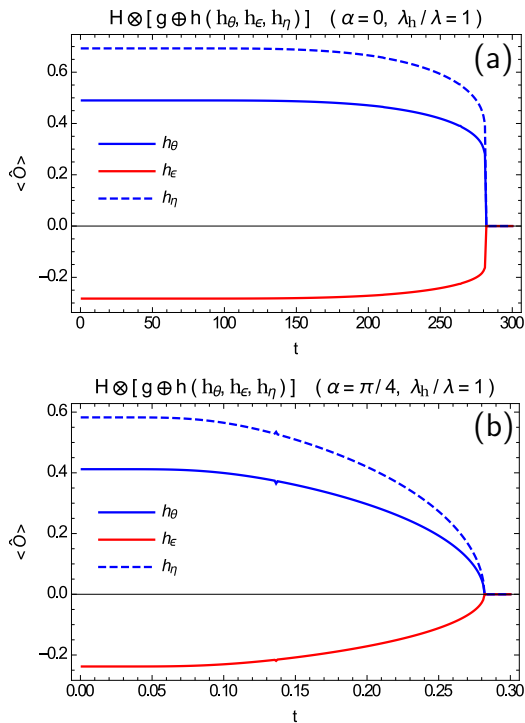


Figure 2. (Color online) The phase diagrams of a cooperative Jahn-Teller phase transition in coordinates h_θ , h_ϵ and h_η of interacting icosahedral clusters. (a) $\alpha = 0$ and (b) $\alpha = \frac{1}{4}\pi$.

5.4. Validity of the mean field theory

We already discussed that the mean field theory is more valid when the fluctuations are small compared to the order parameter or when the interactions are stronger. From the phase diagrams it can be seen that the transitions can be first or second-order depending on the value of α which represents the relative strength of the vibronic coupling. The first-order transitions are those that have stronger vibronic coupling and we expect the mean-field theory to be relatively more valid for these transitions because the fluctuations are small compared to the order parameter near the phase transition and the couplings are stronger [?]. On the other hand, we do not expect high validity of the second-order phase diagrams for the same reasons.

6. Conclusion

We have provided a framework for calculating the characteristics of the cooperative Jahn-Teller phase transition of interacting icosahedral clusters. The formulation of the theory holds for any system of interacting Jahn-Teller centers, although we have specifically calculated the phase diagrams of interacting clusters of icosahedral symmetry. The vibrational modes of molecules of icosahedral symmetry can be coupled to three, four or five-fold degenerate orbitals and we have

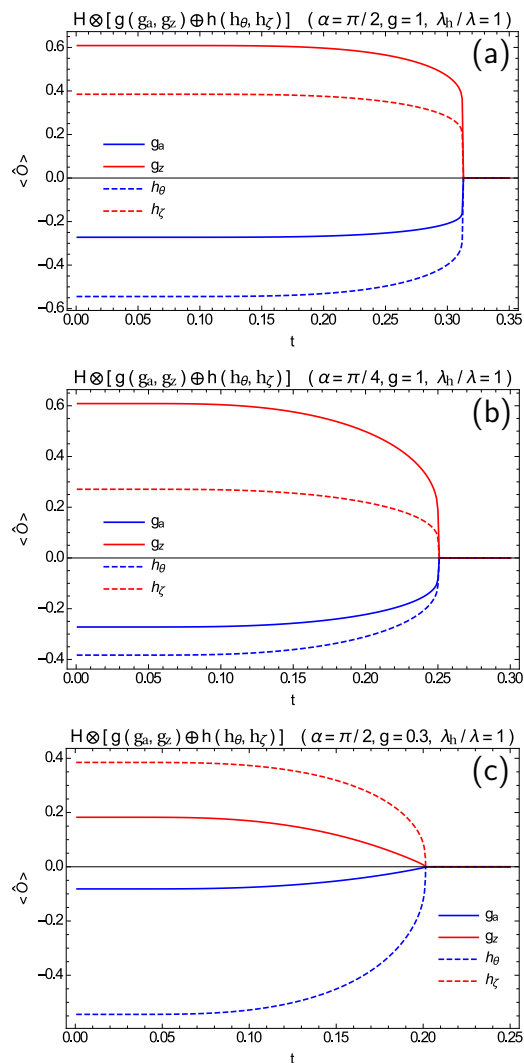


Figure 3. (Color online) Phase diagrams of a cooperative Jahn-Teller phase transition in coordinates g_a , g_z , h_θ and h_ζ of interacting icosahedral clusters. (a) $g = 1, \alpha = \frac{1}{2}\pi$, (b) $g = 1, \alpha = \frac{1}{4}\pi$ and (c) $g = 0.3, \alpha = \frac{1}{2}\pi$

specifically investigated the coupling to five-fold degenerate orbitals, i.e. $H \otimes (g \oplus 2h)$.

An interesting outcome of this work is that the character of the phase transitions depends strongly on the value of the parameter α . To recall, because of the double appearance of the H_g representation in the decomposition of $[H_g \otimes H_g]$, two families of matrices with independent coupling constants are needed to represent the Jahn-Teller effect in such systems. The parameter α measures the relative coupling strength to the two families of matrices. For transitions along the D_{5d} minima, as we increase α from 0 to $\pi/4$, the transition becomes more weakly first-order until it becomes second-order at $\beta = \pi/4$. This observation holds only for the $H \otimes (g \oplus 2h)$ case of the icosahedral

Jahn-Teller phase transitions because of the double appearance of the h representation.

This is the most complicated of all three cases due to the larger size of the vibronic matrix and the double appearance of the representation H_g in the decomposition of the symmetrical direct product of H_g . The $T \otimes H$ is the most studied case, partly because analytical work is more convenient and partly because the anions of C_{60} can undergo such a distortion. The LUMO of C_{60} is three-fold degenerate and, therefore, the excited states and anions of C_{60} have three-fold degeneracy at the Fermi level. The $H \otimes (g \oplus 2h)$ JTE applies to cations of C_{60} since the HOMO of C_{60} is five-fold degenerate. Si_{12} too has five-fold degenerate orbitals at the Fermi level and is distorted by this type of Jahn-Teller effect.

In addition to being able to describe the phase transitions in such systems, this work also serves as a platform for the theory of metallic glass transition and crystallization of metals, where in the liquid phase near the transition temperature the atoms tend to form small non-space-filling clusters of almost icosahedral configuration [?]. These clusters can be treated as Jahn-Teller units with d-orbitals being the highest occupied molecular orbitals. These Jahn-Teller units distort and orient in random directions [?]. Figure ?? shows some of the possible Jahn-Teller distortions of an icosahedral molecular unit. The CJTE is the mechanism by which the distorted clusters align to produce an average order below the transition temperature which can aid the crystallization of the material. On the other hand, the tendency of atoms in forming local icosahedral order will prevent the formation of a crystal due to geometrical frustration. Therefore whether a liquid makes a transition to the crystalline or amorphous phase is really a competition between local and global order.

The geometrical frustration means that there is no single configuration of atoms that minimizes the potential energy [?]. This applies to regular icosahedra because they do not tile the three-dimensional flat space. It is possible that the distorted clusters may be able to tile the space the same way that non-regular pentagons do on a flat surface. However this is difficult to investigate because of the multi-mode nature of the problem. The reduction to one H_g mode means that the new coordinates are not normal any more, but are a linear combination of normal modes [?]. This of course does not apply to the G_g modes which remain normal and their geometrical shapes are simply found by computing the vibrational modes from group theory (by applying projection operators on a vector that initiates from an atom).

Another potential future work is to investigate the geometrical frustration of regular icosahedral units.

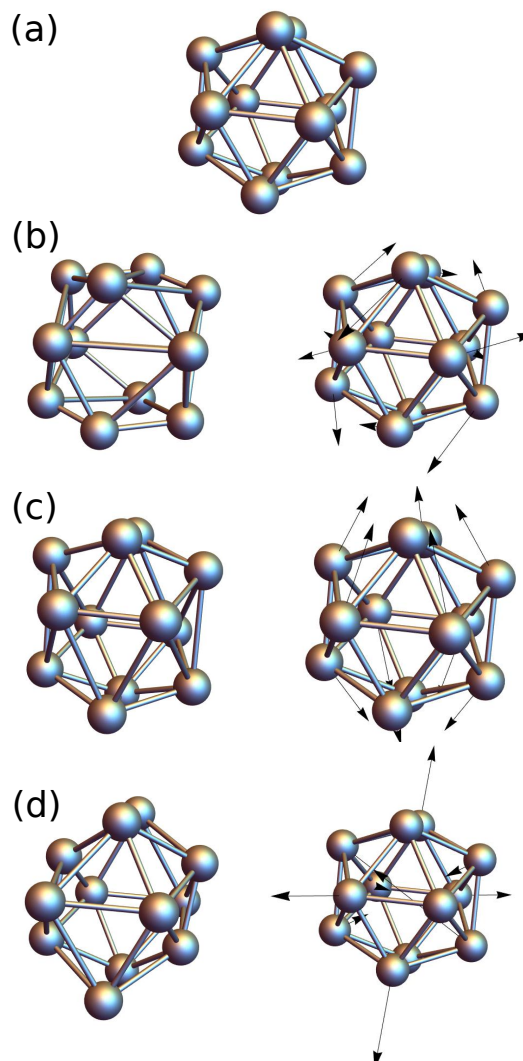


Figure 4. Some of the possible static Jahn-Teller distortions of an icosahedral atomic cluster. The left column shows the actual distorted clusters and the right column is the corresponding direction of movement of atoms from the undistorted configuration. (a) a_{1g} mode (undistorted regular icosahedron), (b) g_g mode, (c and d) h_g modes.

Regular icosahedra can tile on the surface of a four-dimensional hypersphere (polytope $\{3,3,5\}$) [?] and these can be projected on the flat surface which leads to derivation of Landau theories for glasses [?, ?]. They can also be described by disclination which are rotational defects as opposed to dislocations which are translational defects [?].

The Jahn-Teller model derived in this work will be able to describe glasses once the effects of the geometrical frustration of the icosahedral clusters is taken into the model.

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Appendix A. CJTE Hamiltonian

The uniform strain minimizes the Hamiltonian, which yields

$$e_{\Gamma\gamma} = - \sum_{\mathbf{R}} \frac{V_{\Gamma} \widehat{O}_{\Gamma\gamma}(\mathbf{R})}{\Omega\eta_{\Gamma}}. \quad (\text{A.1})$$

Substituting this into Hamiltonian (??) yields,

$$\begin{aligned} H = \sum_{\mathbf{R}\Gamma\gamma} & \left[\frac{P_{\Gamma\gamma}^2(\mathbf{R})}{2M} + \frac{1}{2} M \omega_{\Gamma}^2 Q_{\Gamma\gamma}^2(\mathbf{R}) \right. \\ & + F_{\Gamma} Q_{\Gamma\gamma}(\mathbf{R}) \widehat{O}_{\Gamma\gamma}(\mathbf{R}) \\ & \left. - \sum_{\mathbf{R}'} \frac{V_{\Gamma}^2}{2\Omega\eta_{\Gamma}} \widehat{O}_{\Gamma\gamma}(\mathbf{R}) \widehat{O}_{\Gamma\gamma}(\mathbf{R}') \right]. \quad (\text{A.2}) \end{aligned}$$

The coupling to the strains results in an infinite-range coupling between the clusters.

We now write the coordinates, the conjugate momenta, and the matrices as Fourier series,

$$Q_{\Gamma\gamma}(\mathbf{R}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} q_{\Gamma\gamma}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}}. \quad (\text{A.3})$$

$$P_{\Gamma\gamma}(\mathbf{R}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} p_{\Gamma\gamma}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}}, \quad (\text{A.4})$$

$$\widehat{O}_{\Gamma\gamma}(\mathbf{R}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \widehat{O}_{\Gamma\gamma}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}}, \quad (\text{A.5})$$

and define the transformed ladder operators and coupling constant as:

$$\begin{aligned} a_{\Gamma\gamma}(\mathbf{k}) &= \sqrt{\frac{M\omega_{\Gamma}(\mathbf{k})}{2\hbar}} q_{\Gamma\gamma}(\mathbf{k}) + i \frac{p_{\Gamma\gamma}(\mathbf{k})}{\sqrt{2\hbar M\omega_{\Gamma}(\mathbf{k})}}, \\ a_{\Gamma\gamma}^{\dagger}(-\mathbf{k}) &= \sqrt{\frac{M\omega_{\Gamma}(\mathbf{k})}{2\hbar}} q_{\Gamma\gamma}(\mathbf{k}) - i \frac{p_{\Gamma\gamma}(\mathbf{k})}{\sqrt{2\hbar M\omega_{\Gamma}(\mathbf{k})}}, \quad (\text{A.6}) \\ \xi_{\mathbf{k}}^{\Gamma} &= F_{\Gamma} \sqrt{\frac{\hbar}{2M\omega_{\Gamma}(\mathbf{k})}}. \end{aligned}$$

Substituting the ladder operators into the Hamiltonian and using the fact that $\omega(-\mathbf{k}) = \omega(\mathbf{k})$ due to the symmetry of the system yields,

$$\begin{aligned} H = \sum_{\Gamma,\gamma} & \left[\sum_{\mathbf{k}} \left\{ \hbar\omega_{\Gamma}(\mathbf{k}) \left(a_{\Gamma\gamma}^{\dagger}(\mathbf{k}) a_{\Gamma\gamma}(\mathbf{k}) + \frac{1}{2} \right) \right. \right. \\ & \left. \left. + \xi_{\mathbf{k}}^{\Gamma} \left[a_{\Gamma\gamma}^{\dagger}(-\mathbf{k}) + a_{\Gamma\gamma}(\mathbf{k}) \right] \widehat{O}_{\Gamma\gamma}(-\mathbf{k}) \right\} \right. \\ & \left. - \sum_{\mathbf{R}\mathbf{R}'} \frac{V_{\Gamma}^2}{2\Omega\eta_{\Gamma}} \widehat{O}_{\Gamma\gamma}(\mathbf{R}) \widehat{O}_{\Gamma\gamma}(\mathbf{R}') \right]. \quad (\text{A.7}) \end{aligned}$$

We now transform to displaced coordinates:

$$\gamma_{\Gamma\gamma}^{\dagger}(\mathbf{k}) = \left[a_{\Gamma\gamma}^{\dagger}(\mathbf{k}) + \frac{\xi_{\mathbf{k}}^{\Gamma}}{\hbar\omega_{\Gamma}(\mathbf{k})} \widehat{O}_{\Gamma\gamma}(-\mathbf{k}) \right], \quad (\text{A.8})$$

$$\gamma_{\Gamma\gamma}(\mathbf{k}) = \left[a_{\Gamma\gamma}(\mathbf{k}) + \frac{\xi_{\mathbf{k}}^{\Gamma}}{\hbar\omega_{\Gamma}(\mathbf{k})} \widehat{O}_{\Gamma\gamma}(\mathbf{k}) \right]. \quad (\text{A.9})$$

This is similar to a canonical transformation and has been widely used in the literature [?, ?]. Note that, since the ladder operators are defined in terms of the normal modes of the clusters, the commutation relations are preserved. Inserting the transformed operators into the Hamiltonian yields

$$\begin{aligned} H = \sum_{\Gamma,\gamma} & \left\{ \sum_{\mathbf{k}} \left[\hbar\omega_{\Gamma}(\mathbf{k}) \left(\gamma_{\Gamma\gamma}^{\dagger}(\mathbf{k}) \gamma_{\Gamma\gamma}(\mathbf{k}) + \frac{1}{2} \right) \right. \right. \\ & \left. \left. - \frac{(\xi_{\mathbf{k}}^{\Gamma})^2}{\hbar\omega_{\Gamma}(\mathbf{k})} \widehat{O}_{\Gamma\gamma}(\mathbf{k}) \widehat{O}_{\Gamma\gamma}(-\mathbf{k}) \right] \right. \\ & \left. - \sum_{\mathbf{R}\mathbf{R}'} \frac{V_{\Gamma}^2}{2\Omega\eta_{\Gamma}} \widehat{O}_{\Gamma\gamma}(\mathbf{R}) \widehat{O}_{\Gamma\gamma}(\mathbf{R}') \right\}. \quad (\text{A.10}) \end{aligned}$$

Appendix B. Coordinates and electronic parameters

We take the vibronic interaction as a perturbation to the Hamiltonian. Thus, in a stationary system without displacements, we have,

$$\widehat{H}\phi_m^0 = E_m^0\phi_m^0, \quad (\text{B.1})$$

which, with a vibronic interaction, becomes

$$(\widehat{H} + \lambda\widehat{W})\phi_m = E_m\phi_m. \quad (\text{B.2})$$

As $\lambda \rightarrow 0$, the solution is expressed as a linear combination of the zeroth-order f -fold degenerate wave functions:

$$\lim_{\lambda \rightarrow 0} \phi_m = \sum_{i=1}^f c_i \phi_i^0. \quad (\text{B.3})$$

Degenerate perturbation theory yields the first-order perturbed energy $E^{(1)}$ as,

$$\widehat{W}\mathbf{C} = E^{(1)}\mathbf{C}, \quad (\text{B.4})$$

where \mathbf{C} is the f -dimensional column vector of c_i , from which we obtain

$$E^{(1)} = \mathbf{C}^T \widehat{W} \mathbf{C}.$$

Thus, we may write the general normalized d -orbital wave function as,

$$|\phi\rangle = \theta|\theta\rangle + \epsilon|\epsilon\rangle + \xi|\xi\rangle + \eta|\eta\rangle + \zeta|\zeta\rangle, \quad (\text{B.5})$$

and the total potential energy to first-order in perturbation theory is [?],

$$\begin{aligned} E &= E^0 + E^{(1)} \\ &= \sum_{\Gamma\gamma} \frac{1}{2} M \omega_{\Gamma}^2 Q_{\Gamma\gamma}^2 + \Phi^T \left[\sum_{\Gamma\gamma} \widehat{W}(Q_{\Gamma\gamma}) \right] \Phi, \quad (\text{B.6}) \end{aligned}$$

where $\Phi = (\theta, \epsilon, \xi, \eta, \zeta)^T$. By differentiating the potential energy with respect to each coordinate and setting the result to zero, the extremal coordinates are obtained in terms of the electronic coordinates:

$$\|Q_{\Gamma\gamma}\| = -\frac{1}{M\omega_{\Gamma}^2} \Phi^T \left(\frac{\partial \hat{W}}{\partial Q_{\Gamma\gamma}} \right) \Phi. \quad (\text{B.7})$$

We substitute the equations for extremal coordinates into the potential energy (??) to obtain an expression in terms of only the five electronic parameters.

References

- [1] I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals* (Springer, Berlin, 1989).
- [2] I. B. Bersuker, *The Jahn-Teller Effect* (Cambridge University Press, Cambridge, 2006).
- [3] H. A. Jahn and E. Teller, Proc. R. Soc. Lond. A **161**, 220 (1937).
- [4] J. D. Dunitz and I. E. Orgel, J. Phys. Chem. Solids **3**, 20 (1957).
- [5] D. S. McClure, J. Phys. Chem. Solids **3**, 311 (1957).
- [6] P. J. Wojtovicz, Phys. Rev. **116**, 32 (1959).
- [7] J. Kanamori, J. App. Phys. **31**, S14 (1960).
- [8] R. J. Elliott, G. A. Gehring, A. P. Malozemoff, S. R. P. Smith, W. S. Staude, and R. N. Tyte, J. Phys. C: Solid State Phys. **4**, L179 (1971).
- [9] R. J. Elliott, A. P. Young, and S. R. P. Smith, J. Phys. C: Solid State Phys. **4**, L317 (1971).
- [10] R. J. Elliott, R. T. Harley, W. Hayes, S. R. P. Smith, Proc. R. Soc. Lond. A **328** 217 (1972).
- [11] R. Englman and B. Halperin, Phys. Rev. B **2**, 75 (1970).
- [12] E. Pytte, Phys. Rev. B **3**, 3503 (1971).
- [13] Y. Kino, B. Lüthi, and M. E. Mullen, J. Phys. Soc. Jap. **33**, 687 (1972).
- [14] G. A. Gehring and K. A. Gehring, Rep. Prog. Phys. **38**, 1 (1975).
- [15] V. P. Khlopin, V. Z. Polinger, and I. B. Bersuker, Theoret. Chim. Acta **48**, 87 (1978).
- [16] D. R. Pooler, J. Phys. C: Solid St. Phys. **13**, 1029 (1980).
- [17] A. Ceulemans and P. W. Fowler, Phys. Rev. A **39**, 481 (1989).
- [18] J. P. Cullerne, and M. C. M. O'Brien, J. Phys.: Condens. Matter **6**, 9017 (1994).
- [19] J. P. Cullerne, M. N. Angelova, and M. C. M. O'Brien, J. Phys.: Condens. Matter **7**, 3247 (1995).
- [20] J. L. Dunn, and C. A. Bates, Phys. Rev. B **52**, 5996 (1995).
- [21] J. L. Dunn, M. R. Eccles, Y. Liu, and C. A. Bates, Phys. Rev. B **65**, 115107 (2002).
- [22] M. C. M. O'Brien, Phys. Rev. B **53**, 3775 (1996).
- [23] A. Ceulemans and P. W. Fowler, J. Chem. Phys. **93**, 1221 (1990).
- [24] P. D. Rios and N. Manini, Phys. Rev. B **54**, 7157 (1996).
- [25] C. P. Moate, J. L. Dunn, C. A. Bates and Y. M. Liu, J. Phys.: Condens. Matter **9**, 6049 (1997).
- [26] J. L. Dunn, Phys. Rev. B **69**, 064303 (2004).
- [27] E. A. Moujaes and J. L. Dunn, J. Phys.: Condens. Matter **22**, 085007 (2010).
- [28] R. C. Haddon, L. E. Brus, and K. Raghavachari, Chem. Phys. Lett. **125**, 459 (1986).
- [29] F. A. Cotton, *Chemical Applications of Group Theory* 3rd edn (Wiley, New York, NY, 1990).
- [30] M. S. Dresselhaus, G. Dresselhaus, and A. Jorio, *Group Theory: Application to the Physics of Condensed Matter* (Springer, Berlin, 2008).
- [31] W. Ludwig, C. Falter, *Symmetries in Physics: Group Theory Applied to Physical Problems*, (Springer-Verlag, Berlin, 1996)
- [32] C. C. Chancey and M. C. M. O'Brien, *The Jahn-Teller effect in C₆₀ and other icosahedral complexes*, (Princeton University Press, Princeton., NJ, 1997).
- [33] B. Gu, Z. Li, and J. Zhu, J. Phys.: Condens. Matter **5**, 5255 (1993).
- [34] M. E. Eberhart, K. H. Johnson, D. Adler, R. C. O'Handley, and M. E. McHenry, J. Non-Cryst. Sol. **75** 97 (1985).
- [35] See Supplemental Material for details of the calculations in Secs. ??-??.
- [36] M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill, New York, NY, 1964).
- [37] L. F. Feiner, J. Phys. C: Solid State Phys. **15**, 1495 (1982).
- [38] J. M. Baker, J. Phys. C: Solid St. Phys. **4**, 1631 (1971).
- [39] H. Bruus, K. Flensberg, *Many-Body Quantum Theory in Condensed Matter Physics*, (Oxford University Press, Oxford, 2004)
- [40] P. M. Chaikin, T. C. Lubensky, *Principles of Condensed Matter Physics*, (Cambridge University Press, Cambridge, 1995)
- [41] J. M. Yeomans, *Statistical Mechanics of Phase Transitions*, (Oxford University Press, Oxford, 1992).
- [42] J. C. Slater, *Introduction to Chemical Physics*, (McGraw-Hill, New York, 1939)
- [43] K. A. Dill, S. Bromberg, *Molecular Driving Forces: Statistical Thermodynamics in Biology, Chemistry, Physics, and Nanoscience*, (Garland Science, Taylor & Francis Group, New York, 2011).
- [44] R. J. Naumann, *Introduction to the Physics and Chemistry of Materials*, (CRC Press, Taylor & Francis Group, Boca Raton, 2008)
- [45] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* 3rd edn, (Pergamon, Oxford, 1977).
- [46] U. Öpik and M. H. L. Pryce, Proc. Roy. Soc. **A238** 425 (1957).
- [47] *Mathematica*, Wolfram Research, Inc., Version 10.2, Champaign, IL (2015).
- [48] M. Biskup, L. Chayes, Commun. Math. Phys. **238**, 53 (2003)
- [49] H. W. Sheng, W. K. Luo, F. M. Alamgir, J. M. Bai, and E. Ma, Nature **439**, 419 (2006).
- [50] T. E. Jones, J. Miorelli, and M. E. Eberhart, J. Chem. Phys. **140**, 084501 (2014).
- [51] J. Sadoc, R. Mosseri, *Geometrical Frustration* (Cambridge University Press, Cambridge, 1999).
- [52] D.R. Nelson, M. Widom, Nuclear Physics B **240**, 113 (1984).
- [53] S. Sachdev, D.R. Nelson, Phys. Rev. B, **32**, 1480 (1985).
- [54] D.R. Nelson, Phys. Rev. B **28**, 5515 (1983).
- [55] M. Kataoka and J. Kanamori, J. Phys. Soc. Japan **32**, 113 (1972).