

**PHY 745 Group Theory**  
**11-11:50 AM MWF Olin 102**

**Plan for Lecture 23:**

**Jahn-Teller Effect**  
**Section 7.7 in DDJ**

- 1. Static Jahn-Teller distortion**
- 2. Dynamic Jahn-Teller distortion**
- 3. Example systems**

3/20/2017 PHY 745 Spring 2017 -- Lecture 23 1

---

---

---

---

---

---

---

---

---

---

Fri: 03/10/2017		Spring break - no class		
Mon: 03/13/2017		AFS Meeting - no class		
Wed: 03/15/2017		AFS Meeting - no class		
Fri: 03/17/2017		AFS Meeting - no class		
<b>23 Mon: 03/20/2017</b>	Chap. 7.7	Jahn-Teller Effect	#15	03/24/2017
24 Wed: 03/22/2017				
25 Fri: 03/24/2017				
26 Mon: 03/27/2017				
27 Wed: 03/29/2017				
28 Fri: 03/30/2017				
29 Mon: 04/03/2017				
30 Wed: 04/05/2017				
31 Fri: 04/07/2017				
32 Mon: 04/10/2017				
33 Wed: 04/12/2017				
Fri: 04/14/2017		Good Friday Holiday -- no class		
34 Mon: 04/17/2017				
35 Wed: 04/19/2017				
36 Fri: 04/21/2017				
Mon: 04/24/2017		Presentations I		
Wed: 04/26/2017		Presentations II		

3/20/2017 PHY 745 Spring 2017 -- Lecture 23 2

---

---

---

---

---

---

---

---

---

---

Quantum Theory of materials

Exact Schrödinger equation:

$$\mathcal{H}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) \Psi_{av}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) = E_{av} \Psi_{av}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\})$$

where

$$\mathcal{H}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) = \mathcal{H}^{\text{Nuclei}}(\{\mathbf{R}^a\}) + \mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\})$$

Born-Oppenheimer approximation  
 Born & Huang, *Dynamical Theory of Crystal Lattices*, Oxford (1954)

↓

Approximate factorization:

$$\Psi_{av}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) = X_{av}^{\text{Nuclei}}(\{\mathbf{R}^a\}) \chi_{av}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\})$$

3/20/2017 PHY 745 Spring 2017 -- Lecture 23 3

---

---

---

---

---

---

---

---

---

---

Quantum Theory of materials -- continued

Electronic Schrödinger equation:


$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) \Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) = U_{\alpha}(\{\mathbf{R}^a\}) \Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\})$$

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_{a,\alpha} \frac{Z^a e^2}{|\mathbf{r}_i - \mathbf{R}^a|} + \sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Nuclear Hamiltonian:

$$\mathcal{H}^{\text{Nuclei}}(\{\mathbf{R}^a\}) \chi_{\alpha\nu}^{\text{Nuclei}}(\{\mathbf{R}^a\}) = W_{\alpha\nu} \chi_{\alpha\nu}^{\text{Nuclei}}(\{\mathbf{R}^a\})$$

$$\mathcal{H}^{\text{Nuclei}}(\{\mathbf{R}^a\}) = \sum_a \frac{\mathbf{P}^a{}^2}{2M^a} + U_{\alpha}(\{\mathbf{R}^a\})$$


  
Effective nuclear interaction provided by electrons

3/20/2017 PHY 745 Spring 2017 -- Lecture 23 4

---

---

---

---

---

---

---


---

Consider electronic Hamiltonian

Electronic Schrödinger equation:

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) \Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) = U_{\alpha}(\{\mathbf{R}^a\}) \Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\})$$

$$\mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_{a,\alpha} \frac{Z^a e^2}{|\mathbf{r}_i - \mathbf{R}^a|} + \sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$


  
Electron-electron interaction term prevents exactly separable electron wavefunction

3/20/2017 PHY 745 Spring 2017 -- Lecture 23 5

---

---

---

---

---

---

---

---

Estimate of the error in the Born-Oppenheimer approximation:

$$\left( \mathcal{H}^{\text{Nuclei}}(\{\mathbf{R}^a\}) + \mathcal{H}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) \right) \chi_{\alpha\nu}^{\text{Nuclei}}(\{\mathbf{R}^a\}) \Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\})$$

$$= W_{\alpha\nu} \chi_{\alpha\nu}^{\text{Nuclei}}(\{\mathbf{R}^a\}) \Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) + \Delta_{\alpha}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\})$$

where  $\mathcal{H}^{\text{Nuclei}}(\{\mathbf{R}^a\}) \equiv \sum_a \frac{\mathbf{P}^a{}^2}{2M^a}$

and where  $\Delta_{\alpha}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) = \mathcal{H}^{\text{Nuclei}}(\{\mathbf{R}^a\}) \left( \chi_{\alpha\nu}^{\text{Nuclei}}(\{\mathbf{R}^a\}) \Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\}) \right) - \left( \mathcal{H}^{\text{Nuclei}}(\{\mathbf{R}^a\}) \chi_{\alpha\nu}^{\text{Nuclei}}(\{\mathbf{R}^a\}) \right) \Upsilon_{\alpha}^{\text{Electrons}}(\{\mathbf{r}_i\}, \{\mathbf{R}^a\})$

Because of the electron/nuclear mass ratio,  $\Delta_{\alpha}$  is relatively small. However, **the approximation breaks down when the electronic states are degenerate.**

3/20/2017 PHY 745 Spring 2017 -- Lecture 23 6

---

---

---

---

---

---

---

---

Proceedings of the Royal Society of London. Series A.  
**161**, 220–235 (1937).

### Stability of Polyatomic Molecules in Degenerate Electronic States

#### I—Orbital Degeneracy

BY H. A. JAHN, *Davy-Faraday Laboratory, The Royal Institution*  
 AND E. TELLER, *George Washington University, Washington, D.C.\**

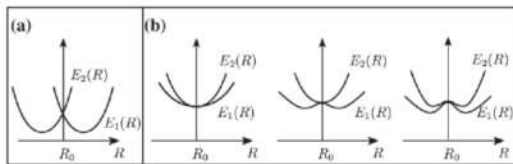
Static and dynamic Jahn-Teller distortion

3/20/2017

PHY 745 Spring 2017 – Lecture 23

7

From Grosso and Pastori Parravicini, Solid State Physics  
 textbook:



**Figure 8.3** Schematic representation of possible topologies of two adiabatic potential-energy surfaces near a degeneracy point  $R_0$  in nuclear coordinate space. In (a) we report the typical Jahn-Teller "conical intersection", with the presence of linear terms in  $R - R_0$ . In (b) we report Renner-Teller "glancing intersections", with the absence of linear terms in  $R - R_0$ , and positive or negative second derivatives. In general, terms linear in certain symmetry-breaking distortions are always possible for any type of degeneracy (except for Kramers degeneracy and some levels in linear molecules).

3/20/2017

PHY 745 Spring 2017 – Lecture 23

8

PHYSICAL REVIEW B **95**, 014108 (2017)

#### First-principles study of the dynamic Jahn-Teller distortion of the neutral vacancy in diamond

Joseph C. A. Prentice,<sup>1</sup> Barisomeu Monserat,<sup>1,2</sup> and R. J. Needs<sup>1</sup>

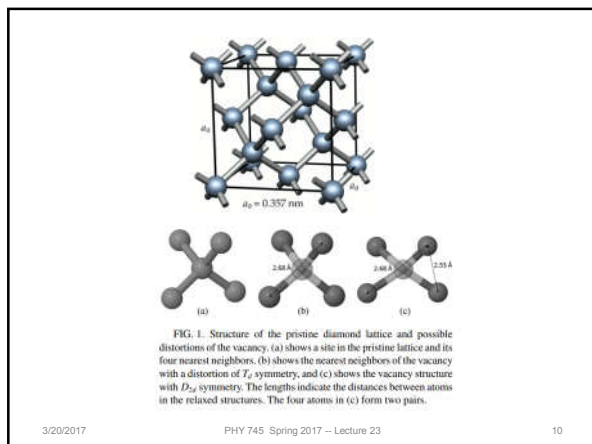
<sup>1</sup>PCM Group, Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom  
<sup>2</sup>Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019, USA  
 (Received 7 October 2016; published 20 January 2017)

First-principles density functional theory methods are used to investigate the structure, energetics, and vibrational motions of the neutral vacancy defect in diamond. The measured optical absorption spectrum demonstrates that the tetrahedral  $T_d$  point group symmetry of pristine diamond is maintained when a vacancy defect is present. This is shown to arise from the presence of a dynamic Jahn-Teller distortion that is stabilized by large vibrational anharmonicity. Our calculations further demonstrate that the dynamic Jahn-Teller-distorted structure of  $T_d$  symmetry is lower in energy than the static Jahn-Teller distorted tetragonal  $D_{2d}$  vacancy defect, in agreement with experimental observations. The tetrahedral vacancy structure becomes more stable with respect to the tetragonal structure by increasing temperature. The large anharmonicity arises mainly from quartic vibrations, and is associated with a saddle point of the Born-Oppenheimer surface and a minimum in the free energy. This study demonstrates that the behavior of Jahn-Teller distortions of point defects can be calculated accurately using anharmonic vibrational methods. Our work will open the way for first-principles treatments of dynamic Jahn-Teller systems in condensed matter.

3/20/2017

PHY 745 Spring 2017 – Lecture 23

9




---

---

---

---

---

---

---

---

---

---

		$T_d (43m)$	$E$	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
$h=24$	$A_1$		1	1	1	1	1
	$A_2$		1	1	1	-1	-1
	$E$		2	-1	2	0	0
	$(R_x, R_y, R_z)$	$T_1$	3	0	-1	-1	1
	$(x, y, z)$	$T_2$	3	0	-1	1	-1

		$D_{2d} (\bar{4}2m)$	$E$	$C_2$	$2S_4$	$2C'_2$	$2\sigma_d$
$h=8$	$R_z$	$A_1$	1	1	1	1	1
		$A_2$	1	1	1	-1	-1
		$B_1$	1	1	-1	1	-1
	$z$	$B_2$	1	1	-1	-1	1
	$(x, y)$	$E$	2	-2	0	0	0
	$(R_x, R_y)$						

→ 3 equivalent  $D_{2d}$  distortions

---

---

---

---

---

---

---

---

---

---

Represent the energy of the vacancy in terms of principal components:

$$E(\mathbf{u}) = E(\mathbf{0}) + \sum_i V_1(u_i) + \frac{1}{2} \sum_{i \neq j} V_2(u_i, u_j). \quad (1)$$

$u_i$  represents amplitude of vibrational mode for wavevector and mode  $(\mathbf{q}, \nu)$ .

Representation of the potential energy surface in the two dominant coordinates

Energy (eV) vs  $u_i (1/\sqrt{2}a_0)$  and  $u_j (1/\sqrt{2}a_0)$

---

---

---

---

---

---

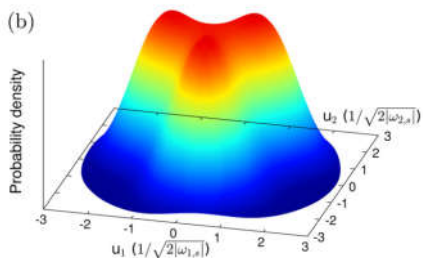
---

---

---

---

Probability density of "dynamic" Jahn-Teller distortion corresponding to lowest energy configuration of this system.



3/20/2017

PHY 745 Spring 2017 -- Lecture 23

13

---

---

---

---

---

---

---

---

---

---

PHYSICAL REVIEW B 91, 214306 (2015)

**Anharmonicity and phase stability of antiperovskite Li<sub>2</sub>OCl**

Min-Hua Chen,<sup>1,2</sup> Alexandra Emly,<sup>1</sup> and Anton Van der Vort<sup>2,\*</sup>

<sup>1</sup>Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA

<sup>2</sup>Materials Department, University of California, Santa Barbara, California 93106, USA

(Received 20 April 2015; revised manuscript received 2 June 2015; published 18 June 2015)

A lattice-dynamics study of the cubic Li<sub>2</sub>OCl antiperovskite, a candidate solid electrolyte in lithium-ion batteries, reveals the presence of dynamical instabilities with respect to rotations of the Li<sub>2</sub>O octahedra. Calculated energy landscapes in the subspace of unstable octahedral rotational modes are very shallow with at most a 1 meV per formula unit reduction in energy upon breaking the cubic symmetry. While Li<sub>2</sub>OCl is not stable relative to decomposition into Li<sub>2</sub>O and LiCl at 0 K, estimates of the vibrational free energy suggest that Li<sub>2</sub>OCl antiperovskite should become entropically stabilized above approximately 480 K.

DOI: 10.1103/PhysRevB.91.214306

PACS number(s): 63.20.dk, 63.70.+h, 63.20.Ry

3/20/2017

PHY 745 Spring 2017 -- Lecture 23

14

---

---

---

---

---

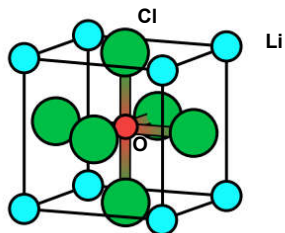
---

---

---

---

---



$Pm\bar{3}m$  space group

3/20/2017

PHY 745 Spring 2017 -- Lecture 23

15

---

---

---

---

---

---

---

---

---

---

