

# $pVT$ relation of $\text{CO}_2$ and the phenomena of critical points

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## I. INTRODUCTION

Molecules are not a solid object with fixed electrons on nuclei. Thus it is evident that when a extra electric field is exerted upon a molecule, the electrons will have a different series of wavefunctions according to the Schrödinger's equation. Considering the electric field as a perturbation, the energy of the system can be expanded in power series of electric field  $E$ , namely

$$H' = H'_0 + \frac{\partial H'}{\partial E}E + \frac{1}{2}\frac{\partial^2 H'}{\partial E^2}E^2 + o(E^2) \quad (1)$$

where  $H'_0$  is the eigenvalue of the energy of the unperturbed system. From another perspective the dipole moment  $\mu$  can be defined as

$$\mu = \int \rho(\mathbf{r})\mathbf{r} d^3\mathbf{r} \quad (2)$$

while the electric potential energy in a constant electric field is

$$U = - \int \rho(\mathbf{r})d\tau(\mathbf{E} \cdot \mathbf{r}) = -\mu \cdot \mathbf{E} \quad (3)$$

When the electric field is in the same direction as the dipole moment, it can be found that

$$\frac{\partial H'}{\partial E} = -\mu \quad (4)$$

For a isotropic system polarizde by a constant electric field, the induced dipole moment is approximately proportional to the electric field, namely

$$\mathbf{p}_{\text{ind}} = \alpha \mathbf{E} \quad (5)$$

where  $\alpha$  is defined as polarizability. For a anisotropic system, the polarizability should be defined as a two-dimensional tensor,

$$\begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \quad (6)$$

or simply

$$p_i = \alpha_i^j E_j \quad (7)$$

in Einstein's notation. With regard to (3), it is observed

$$U' = -\alpha \mathbf{E}^2 \quad (8)$$

thus

$$\alpha = -\frac{1}{2} \frac{\partial^2 H'}{\partial E^2} \quad (9)$$