# Supplemental document

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## S1 Derivation of the electrostatic Hamiltonian

This section is devoted to the evaluation of the electrostatic effective Hamiltonian $H_{\text{es}}$ (*i.e.* Eq. (3) of the text) for the triply degenerate electronic state $\text{T}_{2\text{g}}$ in an octahedral system, which has JT active modes $\text{e}_{\text{g}_\text{i}}$ and $\text{t}_{2\text{g}_\text{i}}$ with $i = 1, 2$. To the best of our knowledge, the derivation of the electrostatic Hamiltonian up to quadratic terms containing bilinear and coupling terms among JT active modes were not reported in the literature. To set up the electrostatic Hamiltonian, we select the following electronic basis set [1]

$$\begin{aligned} \psi_\xi &= \eta\zeta f(r) \\ \psi_\eta &= \xi\zeta f(r) \\ \psi_\zeta &= \xi\eta f(r), \end{aligned} \tag{S1}$$

where $f(r)$ is an exponential or Gaussian radial function.

The electrostatic Hamiltonian $H_{\text{es}}$ was expanded at the reference structure of the $\text{T}_{2\text{g}}$ normal coordinates $\text{Q}_{\epsilon_\text{i}}$, $\text{Q}_{\theta_\text{i}}$, $\text{Q}_{\xi_\text{i}}$, $\text{Q}_{\eta_\text{i}}$ and $\text{Q}_{\zeta_\text{i}}$ for each JT active mode up to second order including all possible coupling between $\text{e}_{\text{g}_\text{i}}$

and $t_{2g_i}$

$$H_{\mathrm{es}} = \sum_{i=1}^{2} \Big[ H^{(1)}_{\epsilon_i} Q_{\epsilon_i} + H^{(1)}_{\theta_i} Q_{\theta_i} + H^{(2)}_{\epsilon_i} Q^2_{\epsilon_i} + H^{(2)}_{\theta_i} Q^2_{\theta_i} + H^{(1)}_{\epsilon_i\theta_i} Q_{\epsilon_i} Q_{\theta_i} \Big]$$
$$+ H^{(1)}_{\epsilon_1\epsilon_2} Q_{\epsilon_1} Q_{\epsilon_2} + H^{(1)}_{\theta_1\theta_2} Q_{\theta_1} Q_{\theta_2} + H^{(1)}_{\epsilon_2\theta_1} Q_{\epsilon_2} Q_{\theta_1} + H^{(1)}_{\theta_2\epsilon_1} Q_{\theta_2} Q_{\epsilon_1}$$
$$+ \sum_{i=1}^{2} \Big[ H^{(1)}_{\xi_i} Q_{\xi_i} + H^{(1)}_{\eta_i} Q_{\eta_i} + H^{(1)}_{\zeta_i} Q_{\zeta_i} + H^{(2)}_{\xi_i} Q^2_{\xi_i} + H^{(2)}_{\eta_i} Q^2_{\eta_i} + H^{(2)}_{\zeta_i} Q^2_{\zeta_i}$$
$$+ H^{(1)}_{\xi_i\zeta_i} Q_{\xi_i} Q_{\zeta_i} + H^{(1)}_{\xi_i\eta_i} Q_{\xi_i} Q_{\eta_i} + H^{(1)}_{\eta_i\zeta_i} Q_{\eta_i} Q_{\zeta_i} \Big] + H^{(1)}_{\xi_1\xi_2} Q_{\xi_1} Q_{\xi_2} + H^{(1)}_{\eta_1\eta_2} Q_{\eta_1} Q_{\eta_2}$$
$$+ H^{(1)}_{\zeta_1\zeta_2} Q_{\zeta_1} Q_{\zeta_2} + H^{(1)}_{\xi_1\zeta_2} Q_{\xi_1} Q_{\zeta_2} + H^{(1)}_{\xi_2\zeta_1} Q_{\xi_2} Q_{\zeta_1} + H^{(1)}_{\xi_1\eta_2} Q_{\xi_1} Q_{\eta_2} + H^{(1)}_{\xi_2\eta_1} Q_{\xi_2} Q_{\eta_1}$$
$$+ H^{(1)}_{\eta_1\zeta_2} Q_{\eta_1} Q_{\zeta_2} + H^{(1)}_{\eta_2\zeta_1} Q_{\zeta_1} Q_{\eta_2}, \tag{S2}$$

where $H^{(1)}_{\tau_i} = \left(\frac{\partial H_{\mathrm{es}}}{\partial Q_{\tau_i}}\right)_0$, $H^{(2)}_{\tau_i} = \frac{1}{2}\left(\frac{\partial^2 H_{\mathrm{es}}}{\partial Q^2_{\tau_i}}\right)_0$ and $H^{(1)}_{\tau_i\tau_j} = \left(\frac{\partial H_{\mathrm{es}}}{\partial^2 Q_{\tau_i} Q_{\tau_j}}\right)_0$. Note that the superscript $\tau_{i,j} \in \{\epsilon_{i,j}, \theta_{i,j}, \xi_{i,j}, \eta_{i,j}, \zeta_{i,j}\}$, where $i$ and $j$ are 1 and 2.

Next step is to calculate the matrix elements of operators of types $H^{(1)}_{\tau_\mathrm{i}} \mathrm{Q}_{\tau_\mathrm{i}}$, $H^{(2)}_{\tau_\mathrm{i}} \mathrm{Q}^2_{\tau_\mathrm{i}}$ and $H^{(1)}_{\tau_\mathrm{i}\tau_\mathrm{j}} \mathrm{Q}_{\tau_\mathrm{i}} \mathrm{Q}_{\tau_\mathrm{j}}$ using electronic basis set of $\mathrm{T_{2g}}$ of Eq. (S1). These matrix elements transform as do the components of the irreducible representation $\mathrm{T_{2g}}$ of the symmetry point group $O_\mathrm{h}$, namely, $\xi$, $\eta$ and $\zeta$. Since $\mathrm{Q}_{\tau_\mathrm{i}}$, $\mathrm{Q}^2_{\tau_\mathrm{i}}$ and $\mathrm{Q}_{\tau_\mathrm{i}} \mathrm{Q}_{\tau_\mathrm{j}}$ do not operate on the electronic basis sets, it is required to calculate matrix elements of $H^{(1)}_{\tau_\mathrm{i}\tau_\mathrm{j}}$, $H^{(2)}_{\tau_\mathrm{i}}$ and $H^{(1)}_{\tau_\mathrm{i}\tau_\mathrm{j}}$. $\mathrm{Q}_{\tau_\mathrm{i}}$, $\mathrm{Q}_{\tau_\mathrm{i}} \mathrm{Q}_{\tau_\mathrm{j}}$ and $\mathrm{Q}^2_{\tau_\mathrm{i}}$ are considered as multiplying factors. For the evaluation of matrix elements, we have used the method described in Ref. [2]. Since operators $H^{(1)}_{\tau_\mathrm{i}\tau_\mathrm{j}}$, $H^{(1)}_{\tau_\mathrm{i}\tau_\mathrm{j}}$ and $H^{(2)}_{\tau_\mathrm{i}}$ have the same transformation properties as $\mathrm{Q}_{\tau_\mathrm{i}}$, $\mathrm{Q}^2_{\tau_\mathrm{i}}$ and $\mathrm{Q}_{\tau_\mathrm{i}} \mathrm{Q}_{\tau_\mathrm{j}}$, we should find irreps and their components according to which the operators $\mathrm{Q}^2_{\tau_\mathrm{i}}$ and $\mathrm{Q}_{\tau_\mathrm{i}} \mathrm{Q}_{\tau_\mathrm{j}}$ transform. This can be understood easily by using the formula of the irreducible products of operators $\mathrm{Q}_{\tau_\mathrm{i}}$ and $\mathrm{Q}_{\tau_\mathrm{j}}$ [2]

$$M^c_\gamma := (\mathrm{Q}^a \times \mathrm{Q}^\mathrm{b})^\mathrm{c}_\gamma = \lambda(\mathrm{c})^{1/2} \sum_{\alpha\beta} \mathrm{V} \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix} \mathrm{Q}^\mathrm{a}_\alpha \mathrm{Q}^\mathrm{b}_\beta, \tag{S3}$$

where := means equal by definition. Note that operators $\mathrm{Q}^\mathrm{a}_\alpha$ and $\mathrm{Q}^\mathrm{b}_\beta$ transform as do components $\alpha$ and $\beta$ of irreducible representations $a$ and $b$, respectively, $V \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}$ coefficients corresponding to the the octahedral group $O_\mathrm{h}$ can be found in Ref. [2]. $\lambda(c)$ is the dimension of irreducible representations $c$ and the sum is over all possible components of $a$ and $b$. For example, in the case of trigonal coordinates $\mathrm{Q}_\xi$, $\mathrm{Q}_\eta$ and $\mathrm{Q}_\zeta$, the sum is over the components triply degenerate irrep $\mathrm{T}_{2g}$ of symmetry group $O_\mathrm{h}$. Note that if $c \in a \times b$, Eq. (S3) spans the irrep $c$, otherwise is zero.

By employing the method described above, we proceed to derive the $\mathrm{T}_{2g} \otimes (\mathrm{t}_{2g} + \mathrm{t}_{2g})$ part of JT problem. For other parts, the same method is applicable. To handle this problem, we first consider the linear terms of the $\mathrm{t}_{2g}$ components of Eq. (S2). In this case, $H^{(1)}_{\tau_\mathrm{i}}$'s transform as $\mathrm{T}_{2g}$. Since operators $H^{(1)}_{\tau_\mathrm{i}}$'s have the same transformation properties as $\mathrm{Q}_{\tau_\mathrm{i}}$ and the coordinate $\mathrm{Q}_{\tau_\mathrm{i}}$'s transforms according to the components of $\xi$, $\eta$ and $\zeta$, thus non-zero matrix elements of linear JT Hamiltonian read

$$\langle\psi_\mu|Q_{\tau_\mathrm{i}}|\psi_\nu\rangle = \kappa_{T_i}|\epsilon_{\alpha\mu\nu}|\mathrm{Q}_{\tau_\mathrm{i}}, \tag{S4}$$

where $\kappa_{T_i}$ is constant and $\epsilon_{\tau\mu\nu}$ is the Levi-Civita symbol, and $\mu$, $\nu$ and $\tau \in \{\xi, \eta, \zeta\}$. Therefore, the non-zero matrix elements are

$$\langle\psi_\xi|Q_{\zeta_\mathrm{i}}|\psi_\eta\rangle = \kappa_{T_i}\mathrm{Q}_{\zeta_\mathrm{i}} \tag{S5}$$

In the next stage, we should consider bilinear terms such as $H^{(1)}_{\alpha_i\beta_i}Q_{\alpha_i}Q_{\beta_i}$. We need to know the transformation properties of $\mathrm{Q}_{\tau_\mathrm{i}}\mathrm{Q}_{\tau_\mathrm{i}}$. This can be understood by using Eq. (S3). Therefore, we have

$$\begin{aligned}
M^{\mathrm{T2g}}_{\xi_\mathrm{i}} &= 2\sqrt{3}V\begin{pmatrix}\mathrm{T}_{2g} & \mathrm{T}_{2g} & \mathrm{T}_{2g}\\ \eta_\mathrm{i} & \zeta_\mathrm{i} & \xi_\mathrm{i}\end{pmatrix}\mathrm{Q}^{\mathrm{T2g}}_{\eta_\mathrm{i}}\mathrm{Q}^{\mathrm{T2g}}_{\zeta_\mathrm{i}} = -\sqrt{2}\left[\mathrm{Q}^{\mathrm{T2g}}_{\eta_\mathrm{i}}\mathrm{Q}^{\mathrm{T2g}}_{\zeta_\mathrm{i}}\right]\\
M^{\mathrm{T2g}}_{\eta_\mathrm{i}} &= 2\sqrt{3}V\begin{pmatrix}\mathrm{T}_{2g} & \mathrm{T}_{2g} & \mathrm{T}_{2g}\\ \xi_\mathrm{i} & \zeta_\mathrm{i} & \eta_\mathrm{i}\end{pmatrix}\mathrm{Q}^{\mathrm{T2g}}_{\xi_\mathrm{i}}\mathrm{Q}^{\mathrm{T2g}}_{\zeta_\mathrm{i}} = -\sqrt{2}\left[\mathrm{Q}^{\mathrm{T2g}}_{\zeta_\mathrm{i}}\mathrm{Q}^{\mathrm{T2g}}_{\xi_\mathrm{i}}\right]\\
M^{\mathrm{T2g}}_{\zeta_\mathrm{i}} &= 2\sqrt{3}V\begin{pmatrix}\mathrm{T}_{2g} & \mathrm{T}_{2g} & \mathrm{T}_{2g}\\ \xi_\mathrm{i} & \eta_\mathrm{i} & \zeta_\mathrm{i}\end{pmatrix}\mathrm{Q}^{\mathrm{T2g}}_{\xi_\mathrm{i}}\mathrm{Q}^{\mathrm{T2g}}_{\eta_\mathrm{i}} = -\sqrt{2}\left[\mathrm{Q}^{\mathrm{T2g}}_{\xi_\mathrm{i}}\mathrm{Q}^{\mathrm{T2g}}_{\eta_\mathrm{i}}\right]
\end{aligned} \tag{S6}$$

Coefficients like $V\begin{pmatrix}\mathrm{T}_{2g} & \mathrm{T}_{2g} & \mathrm{T}_{2g}\\ \xi_\mathrm{i} & \zeta_\mathrm{i} & \eta_\mathrm{i}\end{pmatrix}$ in Eq. (S6) can be found in Ref. [2]. For operators such as $H^{(1)}_{\alpha_\mathrm{i}\beta_\mathrm{j}}\mathrm{Q}_{\alpha_\mathrm{i}}\mathrm{Q}_{\beta_\mathrm{j}}$, we have similar situations. Eq. (S6) tells that the corresponding matrix elements of operators $\mathrm{Q}^{\mathrm{T}_{2g}}_{\eta_\mathrm{i}}\mathrm{Q}^{\mathrm{T}_{2g}}_{\zeta_\mathrm{i}}$, $\mathrm{Q}^{\mathrm{T}_{2g}}_{\xi_\mathrm{i}}\mathrm{Q}^{\mathrm{T}_{2g}}_{\zeta_\mathrm{i}}$ and $\mathrm{Q}^{\mathrm{T}_{2g}}_{\xi_\mathrm{i}}\mathrm{Q}^{\mathrm{T}_{2g}}_{\eta_\mathrm{i}}$ in the diabatic electronic basis $\xi$, $\eta$ and $\zeta$ are proportional to $M^{\mathrm{T2g}}_{\xi_\mathrm{i}}$, $M^{\mathrm{T2g}}_{\eta_\mathrm{i}}$ and $M^{\mathrm{T2g}}_{\zeta_\mathrm{i}}$, respectively. Using this knowledge and the electronic basis set of Eq. (S1) help to evaluate of the matrix elements as follows,

$$\begin{aligned}\langle\psi_\mu|H_{\alpha_i\beta_i}\mathrm{Q}_{\alpha_i}\mathrm{Q}_{\beta_i}|\psi_\nu\rangle &= \langle\mathrm{T_{2g}}|\mathrm{H}_{\alpha_i\beta_i}|\mathrm{T_{2g}}\rangle \mathrm{V}\begin{pmatrix}\mathrm{T_{2g}} & \mathrm{T_{2g}} & \mathrm{T_{2g}}\\ \gamma_i & \alpha_i & \beta_i\end{pmatrix}\mathrm{Q}_{\alpha_i}\mathrm{Q}_{\beta_i}\\ &= \underbrace{\langle\mathrm{T_{2g}}|\mathrm{H}_{\alpha_i\beta_i}|\mathrm{T_{2g}}\rangle(-\frac{1}{\sqrt{6}})}_{B_i}\mathrm{Q}_{\alpha_i}\mathrm{Q}_{\beta_i}\\ &= B_i\mathrm{Q}_{\alpha_i}\mathrm{Q}_{\beta_i} \qquad \text{(S7)}\end{aligned}$$

We have used the following relation in the evaluation of Eq. (S7) [2]:

$$V\begin{pmatrix}\mathrm{T_{2g}} & \mathrm{T_{2g}} & \mathrm{T_{2g}}\\ \gamma & \alpha & \beta\end{pmatrix} = -\frac{1}{\sqrt{6}}|\epsilon_{\gamma\alpha\beta}| \qquad \text{(S8)}$$

If we employ Eq. (S7), the matrix elements in the diabatic electronic basis $\psi_\xi$, $\psi_\eta$ and $\psi_\zeta$ read,

$$\begin{aligned}\langle\psi_\xi|H^{(1)}_{\xi_i\eta_i}\mathrm{Q}_{\xi_i}\mathrm{Q}_{\eta_i}|\psi_\eta\rangle &= B_i\mathrm{Q}_{\xi_i}\mathrm{Q}_{\eta_i}\\ \langle\psi_\xi|H^{(1)}_{\xi_i\zeta_i}\mathrm{Q}_{\xi_i}\mathrm{Q}_{\zeta_i}|\psi_\zeta\rangle &= B_\mathrm{i}\mathrm{Q}_{\xi_i}\mathrm{Q}_{\zeta_i}\\ \langle\psi_\eta|H^{(1)}_{\eta_i\zeta_i}\mathrm{Q}_{\eta_i}\mathrm{Q}_{\zeta_i}|\psi_\zeta\rangle &= B_\mathrm{i}\mathrm{Q}_{\eta_i}\mathrm{Q}_{\zeta_i} \qquad \text{(S9)}\end{aligned}$$

Using Eq. (S9) leads to the following results:

$$\begin{aligned}\langle\psi_\xi|H_{\xi_1\eta_2}Q_{\xi_1}Q_{\eta_2}+H_{\xi_2\eta_1}Q_{\xi_2}Q_{\eta_1}|\psi_\eta\rangle &= b^T(\mathrm{Q}_{\xi_1}\mathrm{Q}_{\eta_2}+\mathrm{Q}_{\xi_2}\mathrm{Q}_{\eta_1})\\ \langle\psi_\xi|H_{\xi_1\zeta_2}Q_{\xi_1}\mathrm{Q}_{\zeta_2}+\mathrm{H}_{\xi_2\zeta_1}\mathrm{Q}_{\xi_2}\mathrm{Q}_{\zeta_1}|\psi_\zeta\rangle &= b^T(\mathrm{Q}_{\xi_1}\mathrm{Q}_{\zeta_2}+\mathrm{Q}_{\xi_2}\mathrm{Q}_{\zeta_1})\\ \langle\psi_\eta|H_{\eta_1\zeta_2}\mathrm{Q}_{\eta_1}\mathrm{Q}_{\zeta_2}+\mathrm{H}_{\zeta_1\eta_2}\mathrm{Q}_{\zeta_1}\mathrm{Q}_{\eta_2}|\psi_\zeta\rangle &= b^T(\mathrm{Q}_{\eta_1}\mathrm{Q}_{\zeta_2}+\mathrm{Q}_{\zeta_1}\mathrm{Q}_{\eta_2}), \qquad \text{(S10)}\end{aligned}$$

where coefficient $b^T$ is proportional to $\langle\mathrm{T_{2g}}|\mathrm{H}_{\alpha_i\beta_i}|\mathrm{T_{2g}}\rangle$. Finally, we should evaluate the corresponding matrix elements of the quadratic terms in Eq.(S2). Strictly speaking, we are interested in terms such as $H^{(2)}_{\alpha_i}{\mathrm{Q}_{\alpha_i}}^2$ and $H^{(1)}_{\alpha_i\alpha_j}\mathrm{Q}_{\alpha_i}\mathrm{Q}_{\alpha_j}$. For the quadratic terms, we should find irreducible representations of $O_\mathrm{h}$ point group of the operators $H^{(2)}_{\alpha_i}$ and $H^{(1)}_{\alpha_i\alpha_j}$. Let consider the irreps $\mathrm{E_g}$ and $\mathrm{A_{1g}}$ and their components and use Eq. (S3). Thus, we have

$$\begin{aligned}M^{\mathrm{E_g}}_{\theta_i} &= \frac{1}{\sqrt{6}}\left[2{\mathrm{Q}_{\zeta_i}}^2-{\mathrm{Q}_{\xi_i}}^2-{\mathrm{Q}_{\eta_i}}^2\right]\\ M^{\mathrm{E_g}}_{\epsilon_i} &= \frac{1}{\sqrt{2}}\left[{\mathrm{Q}_{\xi_i}}^2-{\mathrm{Q}_{\eta_i}}^2\right]\\ M^{\mathrm{A_{1g}}} &= \frac{1}{\sqrt{3}}\left[{\mathrm{Q}_{\xi_i}}^2+{\mathrm{Q}_{\eta_i}}^2+{\mathrm{Q}_{\zeta_i}}^2\right] \qquad \text{(S11)}\end{aligned}$$

Solving Eq. (S11) in terms of $M^{\mathrm{E_g}}_{\theta_\mathrm{i}}$, $M^{\mathrm{E_g}}_{\epsilon_\mathrm{i}}$ and $M^{\mathrm{A_{1g}}}$ yields

$$\begin{aligned}
\mathrm{Q}_{\xi_\mathrm{i}}{}^2 &= \frac{1}{\sqrt{3}}M^{\mathrm{A_{1g}}} - \frac{1}{\sqrt{6}}M^{\mathrm{E_g}}_{\theta_\mathrm{i}} + \frac{1}{\sqrt{2}}M^{\mathrm{E_g}}_{\epsilon_\mathrm{i}} \\
\mathrm{Q}_{\eta_\mathrm{i}}{}^2 &= \frac{1}{\sqrt{3}}M^{\mathrm{A_{1g}}} - \frac{1}{\sqrt{6}}M^{\mathrm{E_g}}_{\theta_\mathrm{i}} - \frac{1}{\sqrt{2}}M^{\mathrm{E_g}}_{\epsilon_\mathrm{i}} \\
\mathrm{Q}_{\zeta_\mathrm{i}}{}^2 &= \frac{2}{\sqrt{6}}M^{\mathrm{E_g}}_{\theta_\mathrm{i}} + \frac{1}{\sqrt{3}}M^{\mathrm{A_{1g}}}.
\end{aligned} \tag{S12}$$

We can repeat this calculation for term such as $H^{(1)}_{\alpha_\mathrm{i}\alpha_\mathrm{j}}$ and summarize the results as follows,

$$\begin{aligned}
\mathrm{Q}_{\xi_1}\mathrm{Q}_{\xi_2} &= \frac{\sqrt{3}}{6}M^{\mathrm{A_{1g}}} - \frac{\sqrt{6}}{12}M^{\mathrm{E_g}}_{\theta_\mathrm{i}} + \frac{1}{2\sqrt{2}}M^{\mathrm{E_g}}_{\epsilon_\mathrm{i}} \\
\mathrm{Q}_{\eta_1}\mathrm{Q}_{\eta_2} &= \frac{\sqrt{3}}{6}M^{\mathrm{A_{1g}}} - \frac{\sqrt{6}}{12}M^{\mathrm{E_g}}_{\theta_\mathrm{i}} - \frac{1}{2\sqrt{2}}M^{\mathrm{E_g}}_{\epsilon_\mathrm{i}} \\
\mathrm{Q}_{\zeta_1}\mathrm{Q}_{\zeta_2} &= \frac{\sqrt{3}}{6}M^{\mathrm{A_{1g}}} + \frac{\sqrt{6}}{6}M^{\mathrm{E_g}}_{\theta_\mathrm{i}}
\end{aligned} \tag{S13}$$

where i can be chosen 1 or 2. Eqs. (S12) and (S13) indicate that the corresponding matrix elements of the operators $H^{(2)}_{\alpha_\mathrm{i}}\mathrm{Q}_{\alpha_\mathrm{i}}{}^2$ and $H^{(1)}_{\alpha_\mathrm{i}\alpha_\mathrm{j}}\mathrm{Q}_{\alpha_\mathrm{i}}\mathrm{Q}_{\alpha_\mathrm{j}}$ are proportional to $M^{\mathrm{E_g}}_{\theta_\mathrm{i}}$,$M^{\mathrm{E_g}}_{\epsilon_\mathrm{i}}$ and $M^{\mathrm{A_{1g}}}$. Thus, non-zero matrix elements of the quadratic terms of Eq. (S2) reads

$$\begin{aligned}
\langle\psi_\xi|H^{(2)}_{\xi_\mathrm{i}}\mathrm{Q}_{\xi_\mathrm{i}}{}^2 + \mathrm{H}^{(2)}_{\eta_\mathrm{i}}\mathrm{Q}_{\eta_\mathrm{i}}{}^2 + \mathrm{H}^{(2)}_{\zeta_\mathrm{i}}\mathrm{Q}_{\zeta_\mathrm{i}}{}^2|\psi_\xi\rangle &= A_\mathrm{i}(2\mathrm{Q}_{\xi_\mathrm{i}}{}^2 - \mathrm{Q}_{\eta_\mathrm{i}}{}^2 - \mathrm{Q}_{\zeta_\mathrm{i}}{}^2) + \frac{\omega_{\mathrm{T_i}}}{2}(\mathrm{Q}_{\xi_\mathrm{i}}{}^2 + \mathrm{Q}_{\eta_\mathrm{i}}{}^2 + \mathrm{Q}_{\zeta_\mathrm{i}}{}^2) \\
\langle\psi_\eta|H^{(2)}_{\xi_\mathrm{i}}\mathrm{Q}_{\xi_\mathrm{i}}{}^2 + \mathrm{H}^{(2)}_{\eta_\mathrm{i}}\mathrm{Q}_{\eta_\mathrm{i}}{}^2 + \mathrm{H}^{(2)}_{\zeta_\mathrm{i}}\mathrm{Q}_{\zeta_\mathrm{i}}{}^2|\psi_\eta\rangle &= A_\mathrm{i}(2\mathrm{Q}_{\eta_\mathrm{i}}{}^2 - \mathrm{Q}_{\xi_\mathrm{i}}{}^2 - \mathrm{Q}_{\zeta_\mathrm{i}}{}^2) + \frac{\omega_{\mathrm{T_i}}}{2}(\mathrm{Q}_{\xi_\mathrm{i}}{}^2 + \mathrm{Q}_{\eta_\mathrm{i}}{}^2 + \mathrm{Q}_{\zeta_\mathrm{i}}{}^2) \\
\langle\psi_\zeta|H^{(2)}_{\xi_\mathrm{i}}\mathrm{Q}_{\xi_\mathrm{i}}{}^2 + H^{(2)}_{\eta_\mathrm{i}}\mathrm{Q}_{\eta_\mathrm{i}}{}^2 + H^{(2)}_{\zeta_\mathrm{i}}\mathrm{Q}_{\zeta_\mathrm{i}}{}^2|\psi_\zeta\rangle &= A_\mathrm{i}(2\mathrm{Q}_{\zeta_\mathrm{i}}{}^2 - \mathrm{Q}_{\xi_\mathrm{i}}{}^2 - \mathrm{Q}^2_{\eta_\mathrm{i}}) + \frac{\omega_{\mathrm{T_i}}}{2}(\mathrm{Q}_{\xi_\mathrm{i}}{}^2 + \mathrm{Q}_{\eta_\mathrm{i}}{}^2 + \mathrm{Q}_{\zeta_\mathrm{i}}{}^2)
\end{aligned} \tag{S14a}$$

$$\begin{aligned}
\langle\psi_\xi|H^{(1)}_{\xi_1\xi_2}\mathrm{Q}_{\xi_1}\mathrm{Q}_{\xi_2} + \mathrm{H}^{(1)}_{\eta_1\eta_2}\mathrm{Q}_{\eta_1}\mathrm{Q}_{\eta_2} + \mathrm{H}^{(1)}_{\zeta_1\zeta_2}\mathrm{Q}_{\zeta_1}\mathrm{Q}_{\zeta_2}|\psi_\xi\rangle &= a^T_1\,(\mathrm{Q}_{\xi_1}\mathrm{Q}_{\xi_2} + \mathrm{Q}_{\eta_1}\mathrm{Q}_{\eta_2} + \mathrm{Q}_{\zeta_1}\mathrm{Q}_{\zeta_2}) + \\
&+ a^T_2\,(2\mathrm{Q}_{\xi_1}\mathrm{Q}_{\xi_2} - \mathrm{Q}_{\eta_1}\mathrm{Q}_{\eta_2} - \mathrm{Q}_{\zeta_1}\mathrm{Q}_{\zeta_2}) \\
\langle\psi_\eta|H^{(1)}_{\xi_1\xi_2}\mathrm{Q}_{\xi_1}\mathrm{Q}_{\xi_2} + \mathrm{H}^{(1)}_{\eta_1\eta_2}\mathrm{Q}_{\eta_1}\mathrm{Q}_{\eta_2} + \mathrm{H}^{(1)}_{\zeta_1\zeta_2}\mathrm{Q}_{\zeta_1}\mathrm{Q}_{\zeta_2}|\psi_\eta\rangle &= a^T_1\,(\mathrm{Q}_{\xi_1}\mathrm{Q}_{\xi_2} + \mathrm{Q}_{\eta_1}\mathrm{Q}_{\eta_2} + \mathrm{Q}_{\zeta_1}\mathrm{Q}_{\zeta_2}) + \\
&+ a^T_2\,(2\mathrm{Q}_{\eta_1}\mathrm{Q}_{\eta_2} - \mathrm{Q}_{\xi_1}\mathrm{Q}_{\xi_2} - \mathrm{Q}_{\zeta_1}\mathrm{Q}_{\zeta_2}) \\
\langle\psi_\zeta|H^{(1)}_{\xi_1\xi_2}\mathrm{Q}_{\xi_1}\mathrm{Q}_{\xi_2} + \mathrm{H}^{(1)}_{\eta_1\eta_2}\mathrm{Q}_{\eta_1}\mathrm{Q}_{\eta_2} + \mathrm{H}^{(1)}_{\zeta_1\zeta_2}\mathrm{Q}_{\zeta_1}\mathrm{Q}_{\zeta_2}|\psi_\zeta\rangle &= a^T_1\,(\mathrm{Q}_{\xi_1}\mathrm{Q}_{\xi_2} + \mathrm{Q}_{\eta_1}\mathrm{Q}_{\eta_2} + \mathrm{Q}_{\zeta_1}\mathrm{Q}_{\zeta_2}) + \\
&+ a^T_2\,(2\mathrm{Q}_{\zeta_1}\mathrm{Q}_{\zeta_2} - \mathrm{Q}_{\xi_1}\mathrm{Q}_{\xi_2} - \mathrm{Q}_{\eta_1}\mathrm{Q}_{\eta_2})
\end{aligned} \tag{S14b}$$

Here, coefficients $A_{\mathrm{i}}$ are proportional to $\langle \mathrm{T_{2g}}|\mathrm{H}^{(2)}_{\Omega_\mathrm{i}}|\mathrm{T_{2g}}\rangle$. Note that coefficients $a^T_{\mathrm{i}} \propto \langle \mathrm{T_{2g}}|\mathrm{H}^{(1)}_{\Omega_\mathrm{i}\Omega_\mathrm{j}}|\mathrm{T_{2g}}\rangle$ where $\Omega_\mathrm{i} \in \{\xi_\mathrm{i}, \eta_\mathrm{i}, \zeta_\mathrm{i}\}$ and $\Omega_\mathrm{j} \in \{\xi_\mathrm{j}, \eta_\mathrm{j}, \zeta_\mathrm{j}\}$ with $i, j = 1, 2$. We used following relations [2]

$$V\begin{pmatrix} \mathrm{E_g} & \mathrm{T_{2g}} & \mathrm{T_{2g}} \\ \theta & \xi & \xi \end{pmatrix} = V\begin{pmatrix} \mathrm{E_g} & \mathrm{T_{2g}} & \mathrm{T_{2g}} \\ \theta & \eta & \eta \end{pmatrix} = -\frac{1}{2}V\begin{pmatrix} \mathrm{E_g} & \mathrm{T_{2g}} & \mathrm{T_{2g}} \\ \theta & \zeta & \zeta \end{pmatrix} = \frac{1}{2\sqrt{3}}$$

$$V\begin{pmatrix} \mathrm{A_{1g}} & \mathrm{b} & \mathrm{b} \\ \mathrm{i} & \beta & \gamma \end{pmatrix} = \lambda(b)^{-1/2}\delta_{\beta\gamma} \tag{S15}$$

where $\lambda(b)$ is the dimension of irreducible representation b and $\delta$ refers to the Kronecker delta.

So far, we discussed how to calculate the matrix elements for the the $\mathrm{T_{2g}} \otimes (\mathrm{t_{2g}} + \mathrm{t_{2g}})$ part of the JT Hamiltonian; Eq. (S4) refers to the matrix elements for linear JT Hamiltonian, Eqs. (S9), (S10) and (S14b) refer to the matrix elements of the bilinear terms. Finally, Eq. (S14a) are the matrix elements for the quadratic terms of the JT Hamiltonian. If one follows the same computational method for the $\mathrm{T_{2g}} \otimes 2\mathrm{e_g}$ part of JT Hamiltonian, the corresponding matrix Hamiltonians for this part JT Hamiltonian will be obtained. For this part of JT Hamiltonian, we did not present the details of calculations and restrict ourselves to the final results for matrix elements. In this way, the electrostatic Hamiltonian $H_{\mathrm{es}}$ can be obtained by the aforementioned matrix elements. The final form of $H_{\mathrm{es}}$ was written down in Appendix A.

# S2 Potential energy surfaces

# References


[1] F. A. Cotton, *Chemical Applications of Group Theory*, ( Wiley-Interscience, New York 1971).

[2] J. S. Griffith, *The Irreducible Tensor Method for Molecular Symmetry Groups* (PRENTICE-HALL, INC, New Jersy, 1962).

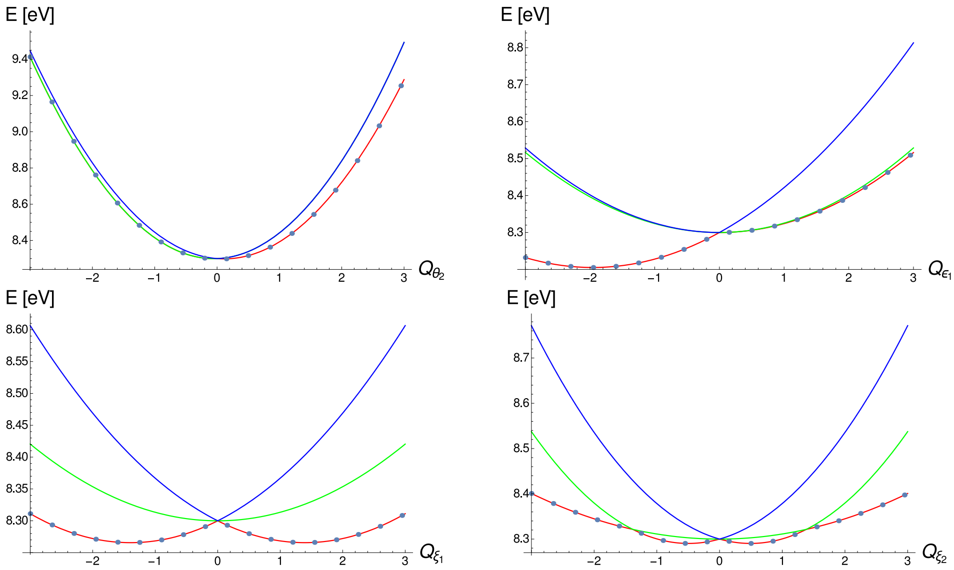


Figure S1: Adiabatic PESs of the $^2T_{2g}$ electronic state of $W(CO)_6^{+\cdot}$ the both components of $e_{g_i}$ modes and $\xi_i$ components of $t_{2g_i}$ modes. The computed DFT data and the corresponding fitted lines are represented by circles and solid lines, respectively.