Supporting Information

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Electronic Structure of the Oxygen Molecule and the Superoxide Ion, O_2^-

Here we briefly review the electronic structure of both the stable electrically neutral (triplet) oxygen molecule and the superoxide ion. In each, we focus on the symmetry transformation properties of the molecular electrons under a π rotation.

First, consider a single neutral oxygen atom, which has eight electrons in the atomic orbitals, $1s_2 2s_2 2p_4$. It is convenient to organize the three 2p orbitals as p_z and $p_\pm = p_x \pm i p_y$, with wavefunctions in spherical coordinates $\psi_{p_z} = \cos(\theta)$ and $\psi_{p_\pm} = e^{\pm i\phi}\sin(\theta)$.

For two oxygen nuclei located at $\vec{R}_\pm = \pm a\hat{z}$, the electronic molecular orbitals in order of increasing energy are the 1s bonding (σ_{1s}), the 1s antibonding (σ_{1s}^*), the 2s bonding orbital (σ_{2s}), the 2s antibonding orbital (σ_{2s}^*), the $2p_z$ bonding orbital (σ_z), the twofold degenerate $2p_\pm$ bonding orbitals ($\Pi_\pm$), the twofold degenerate $2p_\pm$ antibonding orbitals ($\Pi_\pm^*$), and the $2p_z$ antibonding orbital (σ_z^*). The molecular wavefunctions for the $2p_\pm$ antibonding orbitals $\Pi_\pm^*$ are given by

$$\Psi_{\Pi_\pm^*}(\mathbf{r}) = e^{\pm i\phi(x,y)} \sum_{s=\pm 1} s\sin(\theta(z - sa)). \qquad [\text{S1}]$$

The oxygen molecule has 16 electrons, 14 in spin singlet pairs in the seven lowest-energy molecular orbitals ($\sigma_{1s}, \sigma_{1s}^*, \sigma_{2s}, \sigma_{2s}^*, \sigma_z, \Pi_\pm$). We focus on the 2 electrons in the highest occupied molecular orbitals (HOMO) $\Pi_\pm^*$. Due to a molecular Hund's rule, these 2 electrons are in a spin-aligned triplet state with wavefunction

$$\Psi_{\uparrow\uparrow}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}[\Psi_{\Pi_+^*}(\mathbf{r}_1)\Psi_{\Pi_-^*}(\mathbf{r}_2) - \Psi_{\Pi_+^*}(\mathbf{r}_2)\Psi_{\Pi_-^*}(\mathbf{r}_1)],$$
$$[\text{S2}]$$

which has been appropriately antisymmetrized, $\Psi_{\uparrow\uparrow}(\mathbf{r}_1, \mathbf{r}_2) = -\Psi_{\uparrow\uparrow}(\mathbf{r}_2, \mathbf{r}_1)$. From Eq. S1 this wavefunction can be re-expressed as

$$\Psi_{\uparrow\uparrow}(\mathbf{r}_1, \mathbf{r}_2) = \sin(\phi_1 - \phi_2) \sum_{s_1, s_2 = \pm 1} s_1 s_2 \sin(\theta_1)\sin(\theta_2),$$
$$[\text{S3}]$$

with $\phi_j \equiv \phi(x_j, y_j)$ and $\theta_j = \theta(z_j - s_j a)$ for $j = 1, 2$.

We now consider performing a body rotation of the oxygen molecule by 180° about an axis in the x–y plane with unit normal $\hat{n} = \cos(\alpha)\hat{x} + \sin(\alpha)\hat{y}$ for some angle α. Under this transformation, $\phi \to 2\alpha - \phi$ and $\theta \to \pi - \theta$ (equivalently $z \to -z$). Thus, one has $\sin(\phi_1 - \phi_2) \to -\sin(\phi_1 - \phi_2)$ and $\sin(\theta(z - sa)) \to \sin(\theta(z + sa))$, implying that this 180° rotation induces a sign change in the wavefunction for the two HOMO electrons,

$$\Psi_{\uparrow\uparrow}(\mathbf{r}_1, \mathbf{r}_2) \to -\Psi_{\uparrow\uparrow}(\mathbf{r}_1, \mathbf{r}_2). \qquad [\text{S4}]$$

Since the other molecular orbitals are occupied by two (spin-singlet) electrons, each contributes an overall plus sign, either $(+1)^2$ or $(-1)^2$. Thus, under C_2 rotation in triplet molecular oxygen O_2 the electronic states exhibit an overall sign change.

In contrast, for superoxide the two HOMO orbitals are now occupied by three electrons (two in one orbital, say Π_+^*, and the third in Π_-^*). These three electrons carry a net unit of angular momentum aligned along the molecular axis of the oxygen molecule, $J_z = \pm 1$ for the extra electron in the $\Pi_\pm^*$ molecular orbital, respectively. Together with the total electron spin which take on two values, $S_z = \pm 1/2$, the molecule has a fourfold degeneracy $(J_z, S_z) = (\pm 1, \pm 1/2)$. In the presence of spin-orbit interactions $H_{\text{s-o}} = -\lambda \vec{J} \cdot \vec{S}$ this degeneracy is broken, and the molecular ground state is a doublet with $(J_z, S_z) = (1, 1/2)$ and $(J_z, S_z) = (-1, -1/2)$, as required by Kramer's theorem.