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Jahn-Teller effect in density-functional theory

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Jahn and Teller used degenerate perturbation theory to prove that open shell molecules with symmetry Jahn-Teller distort. In that vein, we have developed a perturbative approach to computing Jahn-Teller distortions in Kohn-Sham density-functional theory, starting from a symmetrized molecule with an electronic shell closed by fractional occupation numbers. The resulting highly symmetric state is an energy extremum but not necessarily a minimum. Using second-order perturbation theory, we find the changes in geometry that occur when the symmetry of the electron density is broken to form a state with integer occupation numbers. This methodology allows us to retain many of the computational benefits of working in higher symmetry. As a demonstration, we solve the resulting equations for ten electrons in a superatomlike harmonic-oscillator potential.

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I. INTRODUCTION

Jahn and Teller showed that, except for linear molecules, any open shell molecule with symmetry will distort into a lower symmetry [1]. While these distortions are typically small, they play an important role in molecular and material properties. Jahn-Teller (JT) distortions affect the spacing of orbital eigenvalues, magnetism [2,3], optical properties [4,5], and ligand exchange rates [6], and can also play a role in high-temperature superconductivity [7–9].

While Jahn and Teller's original proof used degenerate perturbation theory (PT) to find the first-order energy associated with symmetry breaking nuclear displacements, no such perturbative description of the JT effect has been developed for Kohn-Sham (KS) [10] density-functional theory (DFT) [11]. The fact that such a method has not previously been formalized is likely in part because degenerate PT for KS DFT was only recently fully developed [12–14]. However, a PT approach for KS DFT would both make a close connection with the original work of Jahn and Teller and allow higher symmetry to be used in molecular geometry optimizations and self-consistent field (SCF) calculations, vastly improving their computational efficiency.

The challenge in translating a perturbative description of the JT effect to KS DFT stems from the nonlinear Coulomb and exchange-correlation (XC) potentials, which break the symmetry of the KS potential unless the electron density is totally symmetric under the molecule's point group. In an open shell molecule, the electron density is not totally symmetric, but it can be symmetrized by using fractional occupation numbers, which also stabilizes the symmetric geometry.

By Janak's theorem [15], such fractionally occupied states are energy extrema, because the first derivative of energy as electrons are moved from one orbital to another is equal to the difference of their eigenvalues. However, the second derivative of energy is typically not zero, and in prior work, we have shown that fractionally occupied solutions can be energy saddle points [13,14]. If this is the case, PT can be used to shift the electrons into a configuration that lowers the energy. This breaks the symmetry of the electron density, and the nuclei respond by breaking the symmetry of the external potential. On the other hand, even if the fractionally occupied state is an energy minimum, moving to an integer occupied state may be desirable for other reasons [16–18].

In this framework, JT distortions appear at second order in degenerate PT as displacements that keep the geometry optimized as the occupation numbers change. We find that, in some ways, the JT problem behaves in the reverse manner of a typical perturbation theory problem. While typically, the perturbing potential selects a particular basis from linear combinations of degenerate orbitals, here, the initial basis of degenerate orbitals picks out particular nuclear displacements from a symmetry-equivalent set.

In Sec. II, we begin with background on KS DFT, fractional occupation numbers, and geometry optimizations, then develop our main equation for calculating JT distortions. In Sec. III, we demonstrate how this equation is simplified by symmetry. In Sec. IV, we apply our equations to a toy model reminiscent of the jellium superatom model of metal clusters [19] including five fractionally occupied d states that are degenerate due to spherical symmetry and a fractionally occupied s state that is "accidentally" degenerate due to a conserved symmetric tensor [20]. Conclusions follow in Sec. V.

II. DERIVATION OF THE METHOD

The total energy of a molecule, E, can be written as a sum of the electronic energy, E_e, and the nuclear-nuclear interaction energy, E_n. In KS DFT, E_e is a functional of the electron density, ρ, so that

$$E[\rho] = E_e[\rho] + E_n. \tag{1}$$

E_n is a function of the nuclear charges and positions, which we denote Z_I and $\mathbf{R}_I$. The vector $\mathbf{R}_I$ has components R_I^α, where α

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can be x, y, or z. We can then write

$$E_n = \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}. \tag{2}$$

Likewise, the nuclear potential is

$$V(\mathbf{r}) = \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|}. \tag{3}$$

The electron density in KS DFT is built from noninteracting molecular orbitals, ϕ_i. Janak introduced orbital occupation numbers, n_i, where $0 \leqslant n_i \leqslant 1$ [15], so that the electron density is given by

$$\rho(\mathbf{r}) = \sum_i n_i\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}), \tag{4}$$

and the electronic energy becomes

$$E_e[\rho] = \sum_i n_i\langle\phi_i| - \frac{1}{2}\nabla^2 - V(\mathbf{r})|\phi_i\rangle + E_{KS}[\rho], \tag{5}$$

where $E_{KS}[\rho]$ is the (direct) Coulomb plus exchange-correlation energy as a functional of ρ.

The condition that E_e is stationary with respect to the orbitals leads to the KS equation

$$H_{\mathrm{KS}}|\phi_i\rangle = \epsilon_i|\phi_i\rangle, \tag{6}$$

$$H_{\mathrm{KS}} = -\tfrac{1}{2}\nabla^2 - V(\mathbf{r}) + \nu_{ks}(\mathbf{r}), \tag{7}$$

where ν_{ks} is the combined Coulomb and XC potential, which is the functional derivative of E_{KS}, and ϵ_i, the orbital eigenvalue, is a Lagrange multiplier that enforces orthonormality.

Whereas in standard quantum mechanics, symmetries of the external potential create degeneracy in the Hamiltonian, the nonlinear Coulomb and XC potentials of standard density functionals only assign H_{KS} a particular symmetry if it is present in both the external potential and the electron density.

If the molecule is closed shell, meaning that all orbitals corresponding to any given irreducible representation of the symmetry group (irrep) are fully occupied, the electron density has the same symmetry as $V(\mathbf{r})$, and H_{KS} has the same degeneracies as the true Hamiltonian. Using fractional occupation numbers, it is possible to turn an open shell system into one that is quasiclosed by equally dividing the available electrons between orbitals within the shell.

The advantage of a closed or quasiclosed shell is that symmetry can be exploited by solving the SCF equations in a basis of symmetry adapted orbitals and optimizing the geometry in symmetry adapted coordinates. The geometry is optimized when the total energy is stationary with respect to nuclear coordinates, so that

$$0 = \frac{\partial E}{\partial R_A^\alpha} = -\sum_i n_i\langle\phi_i|\frac{\partial V(\mathbf{r})}{\partial R_A^\alpha}|\phi_i\rangle + \frac{\partial E_n}{\partial R_A^\alpha}. \tag{8}$$

In closed-shell molecules, the electron density is totally symmetric, and breaking the nuclear symmetry along any given direction must be energetically equivalent to breaking it along any other direction related by a group transformation. Therefore, a closed-shell molecule does not Jahn-Teller distort. If the shell is artificially closed by fractional occupation numbers, finding the true, Jahn-Teller distorted geometry requires transforming the quasiclosed shell solution into an open shell solution. We will do this by relating the changes in a molecule's geometry to changes in its orbital occupation numbers.

A. Maintaining an optimized geometry

According to Janak's theorem [15], the derivative of energy with respect to an orbital occupation number is equal to the orbital's eigenvalue. However, if the nuclear positions are allowed to move as a function of the n_i, the full derivative of E is

$$\frac{\partial E}{\partial n_i} = \epsilon_i - \sum_{A\alpha}\left(\sum_j n_j\langle\phi_j|\frac{\partial V(\mathbf{r})}{\partial R_A^\alpha}|\phi_j\rangle - \frac{\partial E_n}{\partial R_A^\alpha}\right)\frac{\partial R_A^\alpha}{\partial n_i}. \tag{9}$$

By Eq. (8), the term in parentheses is equal to zero at a stationary point of geometry, but, in general, it will not remain so if the occupation numbers are changed. If we wish to remain at a stationary point as the occupation numbers are changed, we must hold the term in parentheses equal to zero, which we can do by allowing the nuclear coordinates to move. To accomplish this, we set the derivative of the term in parentheses with respect to occupation to zero, yielding the equation

$$\begin{aligned} &-\langle\phi_j|\frac{\partial V(\mathbf{r})}{\partial R_A^\alpha}|\phi_j\rangle - 2\,\mathrm{Re}\sum_k n_k\langle\phi_k|\frac{\partial V(\mathbf{r})}{\partial R_A^\alpha}\bigg|\frac{\partial\phi_k}{\partial n_j}\bigg\rangle \\ &+\sum_{B\beta}\Bigg[-\sum_k n_k\bigg(2\,\mathrm{Re}\langle\phi_k|\frac{\partial V(\mathbf{r})}{\partial R_A^\alpha}\bigg|\frac{\partial\phi_k}{\partial R_B^\beta}\bigg\rangle \\ &-\langle\phi_k|\frac{\partial^2 V(\mathbf{r})}{\partial R_A^\alpha\partial R_B^\beta}|\phi_k\rangle\bigg) + \frac{\partial^2 E_n}{\partial R_A^\alpha R_B^\beta}\Bigg]\frac{\partial R_B^\beta}{\partial n_j} = 0. \end{aligned} \tag{10}$$

This is a matrix equation in the indices A and B, having dimension equal to the number of nuclear coordinates. The matrix enclosed in square brackets is the Hessian of the electron-electron interaction energy with respect to the nuclear coordinates, $\mathcal{H}_{AB}^{\alpha\beta}$.

Using the definition of $\rho(\mathbf{r})$ from Eq. (4), we can make the substitutions

$$\frac{\partial\rho(\mathbf{r})}{\partial n_j} \equiv \phi_j^*(\mathbf{r})\phi_j(\mathbf{r}) + 2\,\mathrm{Re}\sum_k \phi_k^*(\mathbf{r})\frac{\partial\phi_k(\mathbf{r})}{\partial n_j}, \tag{11}$$

$$\frac{\partial\rho(\mathbf{r})}{\partial R_B^\beta} \equiv 2\,\mathrm{Re}\sum_k n_k\phi_k^*(\mathbf{r})\frac{\partial\phi_k^*(\mathbf{r})}{\partial R_B^\beta}, \tag{12}$$

so that the Hessian becomes

$$\mathcal{H}_{AB}^{\alpha\beta} = -\int \frac{\partial V(\mathbf{r})}{\partial R_A^\alpha}\frac{\partial\rho(\mathbf{r})}{\partial R_B^\beta} + \frac{\partial^2 V(\mathbf{r})}{\partial R_A^\alpha\partial R_B^\beta}\rho(\mathbf{r})d\mathbf{r} + \frac{\partial^2 E_n}{\partial R_A^\alpha\partial R_B^\beta}, \tag{13}$$

and we can invert it to solve Eq. (10), giving us

$$\frac{\partial R_B^\beta}{\partial n_j} = \sum_{A\alpha}[\mathcal{H}^{-1}]_{AB}^{\alpha\beta}\int\frac{\partial\rho(\mathbf{r})}{\partial n_j}\frac{\partial V(\mathbf{r})}{\partial R_A^\alpha}d\mathbf{r}, \tag{14}$$

where $\mathcal{H}^{-1}$ is the matrix inverse of $\mathcal{H}$.

To obtain the derivatives of $\rho(\mathbf{r})$ in Eqs. (13) and (14), we can use PT. In PT, a function or operator f is expanded order by order in terms of some parameter, λ, in the manner $f = f^{(0)} + \lambda f^{(1)} + \lambda^2 f^{(2)} + \cdots$. The first-order quantity $f^{(1)}$ is the first derivative of f with respect to λ. If we choose the occupation number n_j as our perturbation parameter, then for the nuclear potential, we have

$$V^{(1)} \equiv \sum_{A\alpha} \frac{\partial V(\mathbf{r})}{\partial R_A^\alpha} \frac{\partial R_A^\alpha}{\partial n_j}. \tag{15}$$

For the density, the chain rule tells us

$$\rho^{(1)}(\mathbf{r}) \equiv \sum_{A\alpha} \frac{\partial \rho(\mathbf{r})}{\partial R_A^\alpha} \frac{\partial R_A^\alpha}{\partial n_j} + \frac{\partial \rho(\mathbf{r})}{\partial n_j}, \tag{16}$$

and again, from the chain rule, the first derivative of the Coulomb plus XC potential is

$$v_{ks}^{(1)}(\mathbf{r}) \equiv \int \frac{\delta v_{ks}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \rho^{(1)}(\mathbf{r}') d\mathbf{r}'. \tag{17}$$

Because the systems we are interested in are degenerate, the first-order density has two parts: one from the standard occupied-virtual mixing of coupled-perturbed Kohn-Sham [21–23], and one from mixing of orbitals within the degenerate space. At first order, PT says

$$\langle \phi_i | V^{(1)}(\mathbf{r}) + v_{ks}^{(1)}(\mathbf{r}) | \phi_k \rangle = (\epsilon_k - \epsilon_i) \langle \phi_i | \phi_k^{(1)} \rangle + \epsilon_i^{(1)} \delta_{ik}, \tag{18}$$

which implies that the off-diagonal matrix elements of the first-order perturbing potential vanish when $\epsilon_i = \epsilon_k$.

Substituting in the definitions of $v_{ks}^{(1)}(\mathbf{r})$ and $V^{(1)}(\mathbf{r})$, we get

$$\langle \phi_i | \sum_{A\alpha} \left(\frac{\partial V(\mathbf{r})}{\partial R_A^\alpha} + \int \frac{\delta v_{ks}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \frac{\partial \rho(\mathbf{r}')}{\partial R_A^\alpha} d\mathbf{r}' \right) \frac{\partial R_A^\alpha}{\partial n_j} + \int \frac{\delta v_{ks}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \frac{\partial \rho(\mathbf{r}')}{\partial n_j} d\mathbf{r}' | \phi_k \rangle = \epsilon_i^{(1)} \delta_{ik}, \tag{19}$$

for any degenerate ϕ_i and ϕ_j. Equations (14) and (19) must be solved simultaneously, along with the coupled-perturbed Kohn-Sham equations.

B. Removing off-diagonal elements between accidentally degenerate orbitals

In degenerate PT, the off-diagonal elements of the perturbing potential between degenerate orbitals must be eliminated. In a previous work [14], we showed that these matrix elements behave differently in KS DFT when they are between orbitals from the same irrep than when they are between orbitals from different irreps. Because degenerate orbitals from different irreps tend to have different occupation numbers, they cannot be eliminated by a zeroth-order rotation within the degenerate subspace. Doing so would change the electron density, destroying the SCF solution. Instead, they must be eliminated with a first-order unitary transformation.

Finding this transformation does not involve symmetry considerations. Let us begin by explicitly separating out $\partial\rho/\partial n_j$ and $\partial\rho/\partial R_A^\alpha$ into two parts each. First, we have $\mathbf{U}^{j(1)}$ and $\mathbf{U}^{A(1)}$, which involve first-order unitary transformations between degenerate orbitals. Second, we have the remainder, which we write as $D\rho/Dn_j$ and $D\rho/DR_A^\alpha$. We can then write the derivatives of the density as

$$\frac{\partial \rho(\mathbf{r})}{\partial n_j} = \frac{D\rho(\mathbf{r})}{Dn_j} + 2\,\mathrm{Re} \sum_{kl} n_m \mathbf{U}_{lm}^{j(1)} \phi_l^*(\mathbf{r}) \phi_m(\mathbf{r}), \tag{20}$$

$$\frac{\partial \rho(\mathbf{r})}{\partial R_A^\alpha} = \frac{D\rho(\mathbf{r})}{DR_A^\alpha} + 2\,\mathrm{Re} \sum_{kl} n_m \mathbf{U}_{lm}^{A\alpha(1)} \phi_l^*(\mathbf{r}) \phi_m(\mathbf{r}). \tag{21}$$

With this definition, and using the anti-Hermitian properties of a first-order unitary transformation, we find that Eq. (19) separates into independent equations for $\mathbf{U}^{A(1)}$ and $\mathbf{U}^{j(1)}$,

$$\begin{aligned} \langle \phi_i | \frac{\partial V(\mathbf{r})}{\partial R_A^\alpha} + \int \frac{\delta v_{ks}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \frac{D\rho(\mathbf{r}')}{DR_A^\alpha} d\mathbf{r}' | \phi_k \rangle \\ = -\mathrm{Re} \sum_{lm} \mathbf{U}_{lm}^{A\alpha(1)} (n_m - n_l) \\ \times \langle \phi_i | \int \frac{\delta v_{ks}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \phi_l^*(\mathbf{r}') \phi_m(\mathbf{r}') d\mathbf{r}' | \phi_k \rangle, \end{aligned} \tag{22}$$

$$\begin{aligned} \langle \phi_i | \int \frac{\delta v_{ks}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \frac{D\rho(\mathbf{r}')}{Dn_j} | \phi_k \rangle \\ = -\mathrm{Re} \sum_{lm} \mathbf{U}_{lm}^{j(1)} (n_m - n_l) \\ \times \langle \phi_i | \int \frac{\delta v_{ks}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \phi_l^*(\mathbf{r}') \phi_m(\mathbf{r}') d\mathbf{r}' | \phi_k \rangle. \end{aligned} \tag{23}$$

The solution to Eqs. (22) and (23) can be found by inverting matrices with the composite indices lm and ik, having dimension equal to the number of accidentally degenerate orbitals squared. In essence, we are simply setting $\mathbf{U}_{lm}^{j(1)}$ and $\mathbf{U}_{lm}^{A(1)}$ to whatever values we need to remove unwanted matrix elements.

In addition to removing off-diagonal elements between accidentally degenerate orbitals, we must ensure that we do not introduce new off-diagonal elements when ϕ_i and ϕ_k are from the same irrep. We can do this by using a zeroth-order unitary transformation

$$\langle \phi_i | \mathbf{U}^{(0)\dagger} \int \frac{\delta v_{ks}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \phi_l^*(\mathbf{r}') \phi_m(\mathbf{r}') d\mathbf{r}' \mathbf{U}^{(0)} | \phi_k \rangle = C_i \delta_{ij}, \tag{24}$$

where C_i is some constant.

This transformation only can either be thought of as acting on the bra and ket $\langle \phi_i |$ and $| \phi_k \rangle$ or on ϕ_l^* and ϕ_m and only mixes orbitals from within an irrep. If we allow it to act on ϕ_l^* and ϕ_m, we can absorb it into the first-order unitary transformations, so that

$$\mathbf{U}_{lm}^{A\alpha(1)} \rightarrow \sum_{ab} \mathbf{U}_{al}^{(0)*} \mathbf{U}_{ab}^{A\alpha(1)} \mathbf{U}_{bm}^{(0)}, \tag{25}$$

$$\mathbf{U}_{lm}^{j(1)} \rightarrow \sum_{ab} \mathbf{U}_{al}^{(0)*} \mathbf{U}_{ab}^{j(1)} \mathbf{U}_{bm}^{(0)}, \tag{26}$$

which is simply the rule for a coordinate transformation of matrices. Finding $\mathbf{U}^{A(1)}$ and $\mathbf{U}^{j(1)}$ then becomes a two-step process: first, find a unitary transformation that diagonalizes $\phi_l * \phi_m$ within each irrep. Second, solve Eqs. (22) and (23) and transform these matrices using the first unitary transformation.

III. SIMPLIFICATIONS FROM SYMMETRY

A. Symmetry adapted coordinates

The use of symmetry adapted nuclear coordinates and orbitals greatly simplifies the equations we have developed. We can begin by noting that symmetry adapted nuclear coordinates diagonalize the Hessian of the total energy with respect to nuclear displacements. This has the effect of decoupling the coordinates in Eq. (14), turning it into a series of independent scalar equations.

It can be shown that the Hessian is diagonal in this basis by expanding the molecule's energy to second order in nuclear coordinates to get

$$\begin{aligned} E &\approx E^{(0)} + \sum_{A\alpha} \frac{\partial E}{\partial R_A^\alpha} \delta R_B^\beta + \frac{1}{2} \sum_{A\alpha B\beta} \frac{\partial^2 E}{\partial R_A^\alpha \partial R_B^\beta} \delta R_A^\alpha \delta R_B^\beta \\ &= E^{(0)} + \sum_{A\alpha} \frac{\partial E}{\partial R_A^\alpha} \delta R_A^\alpha + \frac{1}{2} \sum_{A\alpha B\beta} \mathcal{H}_{AB}^{\alpha\beta} \delta R_A^\alpha \delta R_B^\beta. \end{aligned} \tag{27}$$

Because the electron density has the same symmetry as the nuclei, E is invariant under a group operation on the nuclei. Therefore, each term in its Taylor series must be invariant under a group operation as well. This implies that the eigenvalues of $\mathcal{H}$ are equal within each irrep, and it follows that $\mathcal{H}$ is diagonalized by symmetry-adapted coordinates.

We will refer to the symmetry adapted nuclear coordinates with the convention $S_{t\gamma}^m$, where the greek index (γ in this case) runs over irreps, the index t distinguishes different sets of coordinates that transform as γ, and m picks out a specific element of the representation.

Likewise, we will refer to symmetry adapted molecular orbitals as $\phi_{s\gamma}^m$, where again s distinguishes different sets of orbitals that transform as γ (e.g., $2p$ and $3p$ orbitals, which cannot be group-theoretically distinguished). As with the nuclear coordinates, the symmetry adapted orbitals can be produced from a unitary transformation on the original orbitals. In this notation, Eq. (14) becomes

$$\frac{\partial S_{t\gamma}^l}{\partial n_{u\sigma}^m} = \frac{1}{\mathcal{H}_{t\gamma}} \int \frac{\partial \rho(\mathbf{r})}{\partial n_{u\sigma}^m} \frac{\partial V(\mathbf{r})}{\partial S_{t\gamma}^l} d\mathbf{r}, \tag{28}$$

where we have now used only one index for $\mathcal{H}$ because it is diagonal. Because the eigenvalues of the Hessian are equal within each irrep, we have additionally removed the superscript m. This will become important in the section below, because we will diagonalize $V^{(1)}$ by mixing nuclear coordinates from within an irrep, which leaves the Hessian unchanged.

B. Diagonalizing the nuclear potential

Symmetry also simplifies the diagonalization of the perturbing potential within the degenerate subspace for Eq. (19). Typically, this would be done by applying a unitary transformation that mixes the degenerate orbitals [24]. However, in this case, the perturbing potential is unknown because it depends on the nuclear displacements given by $\partial S_{t\gamma}^l / \partial n_j$ from Eq. (14). Further complicating matters, the perturbing Coulomb and XC potentials depend on the first-order orbitals, which are also unknown until the perturbation equations are solved.

To find a remedy for this, we will begin by looking at only the perturbing nuclear potential. Later, we will see that, once it is diagonalized, this will automatically diagonalize Coulomb and XC potentials as well, but for the moment, we will simply ignore them.

We start by noting that there is some unitary transformation $\mathbf{U}$ that diagonalizes the perturbing nuclear potential within a given irrep. This is done by rotating orbitals from within that irrep into one another to create a new, equivalent basis.

Next, take the expectation value of an operator, $\mathbf{O}_\alpha^m$, belonging to an irrep α, in this basis. Because $\mathbf{O}_\alpha^m$ belongs to an irreducible representation of the symmetry group, like $\mathbf{U}$, it does not mix orbitals from different irreps. Since neither $\mathbf{U}$ nor $\mathbf{O}_\alpha^m$ mix orbitals from different irreps, we can combine them into a single operator that also belongs to α. In other words,

$$\langle \phi_{t\gamma}^l | \mathbf{U}^\dagger \mathbf{O}_\alpha^l \mathbf{U} | \phi_{u\beta}^n \rangle = \langle \phi_{t\gamma}^l | (\mathbf{U}^\dagger \mathbf{O}_\alpha^m \mathbf{U})_\alpha | \phi_{u\beta}^n \rangle, \tag{29}$$

$$\mathbf{O}'^m_\alpha = (\mathbf{U}^\dagger \mathbf{O}_\alpha^m \mathbf{U})_\alpha. \tag{30}$$

Because this new operator also belongs to α, it can be written as a linear combination of operators from the original representation of α as

$$\mathbf{O}'^m_\alpha = \sum_n \mathbf{U}_\alpha^{mn} \mathbf{O}_\alpha^n. \tag{31}$$

Now we apply this result to the nuclear perturbing potential, $\partial V / \partial S_{u\beta}^j$, which is an operator that transforms according to the irreducible representation β of the symmetry group. Again, because the unitary transformation we applied to diagonalize it does not mix irreps, we can write it as the coordinate transformation

$$\frac{\partial V}{\partial S_{u\beta}^q} \rightarrow \sum_k \mathbf{U}_\beta^{qk} \frac{\partial V}{\partial S_{u\beta}^k}. \tag{32}$$

The interpretation of this operation is straightforward: in a given point group, there are many symmetry equivalent directions. A Jahn-Teller distortion in one particular direction is indistinguishable from a Jahn-Teller distortion in another symmetry equivalent direction. By choosing a coordinate system in which the nuclear perturbing potential is diagonal, we are allowing the orbital basis we have chosen to pick out compatible directions for our molecule to distort along out of the symmetry equivalent set.

In general, the number of off-diagonal matrix elements that we wish to set equal to zero is different from the number of rotation angles between the various $S_{u\beta}^k$. Therefore, the number of unknown parameters is different from the number of equations that can by generated by requiring the off diagonal matrix elements to vanish.

One approach to finding the matrix $\mathbf{U}_\beta^{qk}$ in light of this difficulty is to minimize the sum of the squares of the off diagonal matrix elements, which results in the equation

$$\frac{\partial}{\partial \mathbf{U}_\beta^{qk}} \sum_{i>j} \left(\sum_k \mathbf{U}_\beta^{qk} \langle \phi_{t\gamma}^i | \frac{\partial V}{\partial S_{u\beta}^k} | \phi_{t\gamma}^j \rangle \right)^2 = 0. \tag{33}$$

Taking the derivative, we find that the $\mathbf{U}_{\beta}^{qk}$ are the zero-eigenvectors of the matrix with indices p, k,

$$\sum_{i>j} \langle \phi_{t\gamma}^{i} | \frac{\partial V}{\partial S_{u\beta}^{p}} | \phi_{t\gamma}^{j} \rangle \langle \phi_{t\gamma}^{j} | \frac{\partial V}{\partial S_{u\beta}^{k}} | \phi_{t\gamma}^{i} \rangle, \tag{34}$$

for every u, β and for the t and γ at the Fermi level. If the Fermi level spans multiple t or γ, the zero eigenvectors of the largest irrep can be used, and unitary transformations can be applied to orbitals in the other irreps to diagonalize the potential. Note that the number of zero eigenvectors is usually smaller than the dimension of the matrix in Eq. (34). This is what we should expect, because for a given β, we are picking out a subset of coordinates that excludes symmetry-equivalent directions.

C. Diagonalizing the Coulomb and XC potentials

Once the first-order nuclear potential is diagonalized within the degenerate subspace, symmetry requirements force the first-order Coulomb and XC potentials to automatically be diagonalized as well. To prove this, we will first look at the symmetry of the unperturbed potentials, and then determine how changes in the electron density affect this symmetry.

Because the unperturbed density is quasiclosed shell, $v_{ks}(\mathbf{r})$ belongs to the totally symmetric representation of the point group. Potentials belonging to the totally symmetric representation are automatically diagonal within a given irreducible representation. If we change the orbital occupation numbers at the Fermi level, the nuclear coordinates move slightly in response. The full first derivative of the density with respect to occupation numbers from Eq. (11) is

$$\rho^{(1)}(\mathbf{r}) = \sum_{c\sigma v} \frac{\partial \rho(\mathbf{r})}{\partial S_{c\sigma}^{v}} \frac{\partial S_{c\sigma}^{v}}{\partial n_{s\gamma}^{m}} + \frac{\partial \rho(\mathbf{r})}{\partial n_{s\gamma}^{m}}, \tag{35}$$

and the response of the Coulomb and XC potentail is given by Eq. (17).

The Coulomb and XC kernel, $\delta v_{ks}(\mathbf{r})/\delta \rho(\mathbf{r}')$, which appears in $v_{ks}^{(1)}$, has the same symmetry as $v_{ks}(\mathbf{r})$. The off-diagonal matrix elements of $v_{ks}^{(1)}$ are therefore determined by the symmetries of $\rho^{(1)}$.

To determine the symmetries of $\rho^{(1)}$, we can employ first-order PT, which tells us [25]

$$\rho^{(1)} = 2\,\mathrm{Re} \sum_{a\mu i b\nu j} (n_{a\mu} - n_{b\nu}) \phi_{b\nu}^{*j} \phi_{a\mu}^{i} \frac{\langle \phi_{b\nu}^{j} | V^{(1)} + v_{ks}^{(1)} | \phi_{a\mu}^{i} \rangle}{\epsilon_{a\mu} - \epsilon_{b\nu}} + \rho_{\mathrm{degen}}^{(1)} + \phi_{s\gamma}^{*m} \phi_{s\gamma}^{m}, \tag{36}$$

where $\rho_{\mathrm{degen}}^{(1)}$ is the contribution to the density from degenerate PT described in Sec. II B,

$$\rho_{\mathrm{degen}}^{(1)} = \mathrm{Re} \sum_{\substack{mn \\ s\gamma t\beta}} (n_{s\gamma} - n_{t\beta}) \times \left(\mathbf{U}_{s\gamma t\beta}^{n(1)mn} + \sum_{c\sigma v} \mathbf{U}_{s\gamma t\beta}^{C(1)mn} \frac{\partial S_{c\sigma}^{v}}{\partial n_{s\gamma}^{m}} \right) \phi_{s\gamma}^{*m} \phi_{t\beta}^{n}, \tag{37}$$

and, as in Eq. (15), for compactness we have defined

$$V^{(1)} \equiv \sum_{c\sigma v} \frac{\partial V(\mathbf{r})}{\partial S_{c\sigma}^{v}} \frac{\partial S_{c\sigma}^{v}}{\partial n_{s\gamma}^{m}}. \tag{38}$$

The initial occupation numbers within any irrep are equal, as are the eigenvalues, so we have labeled each with only two indices, e.g., $n_{a\mu}$ and $\epsilon_{a\mu}$. An extra index appears in $\partial S_{c\sigma}^{v}/\partial n_{s\gamma}^{m}$, because we are shifting the occupation numbers away from the totally symmetric configuration.

We showed in the previous section how $\rho_{\mathrm{degen}}^{(1)}$ can be diagonalized, which leaves only the first and third terms on the right-hand side of Eq. (36) that need to be investigated. Before tackling the first term, which involves a sum over states, let us look at the third term, $\phi_{s\gamma}^{*m}(\mathbf{r})\phi_{s\gamma}^{m}(\mathbf{r})$. It is easy to show that this term is diagonal within any degenerate shell by rewriting its matrix elements as the inner product of two product-representation vectors,

$$\langle \phi_{a\sigma}^{n} | \phi_{s\gamma}^{*m} \phi_{s\gamma}^{m} | \phi_{a\sigma}^{p} \rangle = \langle \phi_{s\gamma}^{m} \phi_{a\sigma}^{n} | \phi_{s\gamma}^{m} \phi_{a\sigma}^{p} \rangle. \tag{39}$$

The two product-representation vectors can be decomposed into their irreducible representations, using Clebsch-Gordan coefficients, as

$$\langle t\alpha q | \phi_{s\gamma}^{m} \phi_{a\sigma}^{p} \rangle = \langle t\alpha q | \gamma m; \sigma p \rangle f_{s\gamma a\sigma}(\mathbf{r}), \tag{40}$$

where the right-hand side is a Clebsch-Gordan coefficient multiplied by a radial function, $f_{s\gamma a\sigma}(\mathbf{r})$. The index t picks out a particular copy of α if the irreducible representation α appears more than once in $\gamma m \sigma p$.

Because of the orthogonality of different irreducible representations, the inner product between the two vectors becomes

$$\sum_{t\alpha q} \langle \gamma m; \sigma p | t\alpha q \rangle \langle t\alpha q | \gamma m; \sigma n \rangle \int f_{s\gamma a\sigma}(\mathbf{r})^{2} d\mathbf{r}. \tag{41}$$

One of the orthogonality relations of Clebsch-Gordan coefficients tells us that

$$\sum_{t\alpha q} \langle \sigma n; \gamma m | t\alpha q \rangle \langle t\alpha q | \sigma p; \gamma j \rangle = \delta_{np} \delta_{nj} \tag{42}$$

and, employing this, we are left with

$$\langle \phi_{s\gamma}^{m} \phi_{a\sigma}^{p} | \phi_{s\gamma}^{m} \phi_{a\sigma}^{n} \rangle = \delta_{mm} \delta_{np} \int f_{s\gamma a\sigma}(\mathbf{r})^{2} d\mathbf{r}, \tag{43}$$

which is clearly diagonal in the indices n and p.

The remaining terms in Eq. (36) are complicated by the fact that there is an implicit dependence of $\rho^{(1)}$ on itself, through the term $v_{ks}^{(1)}$ on the right-hand side. If this term is moved to the left-hand side, $\rho^{(1)}$ can be found through a matrix inversion [25], although typically an iterative process is used instead. Looking more closely at the iterative process will give us insight into the symmetry of the first-order density and KS potential.

We can express the iterative solution for the first-order density like so: define the potential $\mathcal{V}_N$ to be $-V^{(1)} + v_{ksN}^{(1)}$, where $v_{ksN}^{(1)}$ is the first-order Coulomb and XC potential generated after N iterations, and $\nu_{ks0} = 0$. We can then write

$$\rho^{(1)}_{N+1} = 2\,\mathrm{Re}\sum_{a\mu ib\nu j}(n_{a\mu} - n_{b\nu})\phi^{*j}_{b\nu}\phi^{i}_{a\mu}\frac{\langle\phi^{j}_{b\nu}|\mathcal{V}_N|\phi^{i}_{a\mu}\rangle}{\epsilon_{a\mu} - \epsilon_{b\nu}} + \rho^{(1)}_{\mathrm{degen}} + \phi^{*m}_{s\gamma}\phi^{m}_{s\gamma}. \tag{44}$$

After obtaining, the density $\rho^{(1)}_{N+1}$, it is then used to generate $\nu^{(1)}_{ksN+1}$, and the process is repeated. In the limit that $N \to \infty$, the result is a geometric series, which converges to the appropriate matrix inverse to produce $\rho^{(1)}$.

We will show that if $\mathcal{V}_N$ is diagonal within the degenerate subspace, then $\mathcal{V}_{N+1}$ is as well. Because $\mathcal{V}_0 = V^{(1)}$, which we have already diagonalized, we then have a proof by induction.

The potential $\mathcal{V}_N$ can be written in terms of components that transform according to different irreducible representations of the symmetry group, which we label $\mathcal{V}^{q}_{Nt\beta}$, using the same notation as for the orbitals and nuclear coordinates. The matrix elements of $\mathcal{V}^{q}_{Nt\beta}$ can be obtained from the Wigner-Eckart theorem as

$$\sum_{k}\langle k\nu j|\beta q;\mu i\rangle\langle\phi_{b\nu}||\mathcal{V}_{Nt\beta}||\phi_{a\mu}\rangle_k, \tag{45}$$

which is a sum over products of Clebsch-Gordan coefficients and reduced matrix elements. The Clebsch-Gordan coefficients project the product representation of $\mathcal{V}^{q}_{Nt\beta}$ and $\phi^{i}_{a\mu}$ onto the irreducible representation ν.

The matrix elements of $\mathcal{V}^{q}_{Nt\beta}$ are integrals of a product of three functions: two orbitals and a potential. But because $\mathcal{V}^{q}_{Nt\beta}$ commutes with the position operator, the ordering of these three functions in the integrand is arbitrary. Therefore, as Jahn and Teller did [1], we can equivalently write our matrix elements in such a way that we project the product representation of $\phi^{*j}_{b\nu}\phi^{i}_{a\mu}$ onto the irreducible representation β. Doing so, Eq. (45) becomes

$$\sum_{k}\langle k\beta q|\nu j;\mu i\rangle\langle\phi_{b\nu}||\mathcal{V}_{Nt\beta}||\phi_{a\mu}\rangle_k. \tag{46}$$

We can substitute this expression for the matrix elements into Eq. (44) and project the entire thing onto its irreducible components to get

$$\sum_{\substack{a\mu ib\nu j\\ t\beta qk}}\frac{\langle s\alpha r|\nu j;\mu i\rangle\langle\mu i;\nu j|\beta qk\rangle}{\epsilon_{a\mu} - \epsilon_{b\nu}}\langle\phi_{b\nu}||\mathcal{V}_{Nt\beta}||\phi_{a\mu}\rangle_k \times f_{a\mu b\nu}(\mathbf{r}). \tag{47}$$

We can now employ another Clebsch-Gordan orthogonality condition, which says

$$\sum_{ij}\langle s\alpha r|\nu j;\mu i\rangle\langle\mu i;\nu j|k\beta q\rangle = \delta_{ks}\delta_{\alpha\beta}\delta_{qm}. \tag{48}$$

Because the sum is over i and j, and the eigenvalues and reduced matrix elements in Eq. (47) are independent of i and j, we find

$$\rho^{(1)}_{N+1} = \delta_{ks}\delta_{\beta\gamma}\delta_{qm}\sum_{\mu\nu}\frac{\langle\nu||\mathcal{V}_{Nt\beta}||\mu\rangle_k}{\epsilon_{a\mu} - \epsilon_{b\nu}}f_{a\mu b\nu}(\mathbf{r}) + \rho^{(1)}_{\mathrm{degen}} + \phi^{*m}_{s\gamma}\phi^{m}_{s\gamma}. \tag{49}$$

This says that $\rho^{(1)}_{N+1}$ (and by extension, $\mathcal{V}_{N+1}$) can be written in the same basis of irreducible elements as $\mathcal{V}_N$, plus two additional terms that we have already shown are properly diagonalized. To understand the implications, remember that we diagonalized $V^{(1)}$ by choosing a basis of states that are diagonal within the degenerate subspace of the symmetry group. Because $\mathcal{V}_N$ can be written in this same basis for arbitrary N, $\nu^{(1)}_{ks}$ must be diagonal as well.

IV. APPLICATION TO A TOY MODEL

To further investigate the structure of our equations and demonstrate them in practice, we turn to a simple toy model of ten electrons in a harmonic-oscillator potential, $-V(\mathbf{r}) = 1/2\omega^2\mathbf{r}^2$. The local charge density that produces this potential can be found from its Laplacian,

$$\nabla^2\left(\frac{1}{2}\omega^2\mathbf{r}^2\right) = 3\omega^2. \tag{50}$$

This uniform, positive, jellium charge distribution is sometimes used to model the nuclear potential in large metal clusters [19]. In that vein, we can think of our toy model as describing the Jahn-Teller distortions of a so-called "superatom": a sphere of uniform charge density. With the series of approximations we will make, the actual physical analogy is weak; however, the model is still sufficient, because our purpose is not to shed light on any real system but to provide some context for the equations we have developed.

Our first simplification will be to assume that the radius of the superatom is very large, taking the limit that it goes to infinity. Second, we take the limit that the oscillator frequency, ω, becomes infinite, so that the Coulomb and XC potentials are small in comparison to the external potential, and our unperturbed orbitals are well described by eigenvectors of

$$\left(-\frac{1}{2}\nabla^2 + \frac{1}{2}\omega^2\mathbf{r}^2\right)|\phi_i\rangle = \epsilon_i|\phi_i\rangle. \tag{51}$$

If the superatom is distorted, its total charge and dipole moment will remain unchanged, and the lowest-order change to the external potential is its quadrupole moment. However, the expansion of the external potential as a monopole plus a quadrupole is only valid outside of the superatom, and the effects of the distortion diminish as we approach the center of charge. In fact, because we have taken the limit that the superatom's radius is infinite, the nuclear potential and total energy are unaffected by Jahn-Teller distortions.

To solve this, we cut out a spherical hole in the center of our superatom. This acts like a region of negative charge with charge density $-3\omega^2$ sitting on top of the positively charged background. The total charge q of a hole with radius R_0 is then

$$q = -4\pi R_0^3\omega^2, \tag{52}$$

and distortions of this hole generate a quadrupole potential. We will assume that R_0 is small so that our harmonic-oscillator solutions are still valid for the unperturbed orbitals.

The three-dimensional harmonic oscillator has spherical symmetry and it's eigenstates are the product of a radial function $F_k(\mathbf{r})$ with the spherical harmonics Y^m_ℓ. Spherical symmetry requires that the energy is independent of m, which ranges from $-\ell$ to ℓ. However, deeper symmetries [20,26] produce additional degeneracies, and the eigenvalues are given by

$$\epsilon_{k\ell} = \left(2k + \ell + \frac{3}{2}\right)\omega. \tag{53}$$

Unlike the hydrogen atom, ℓ is independent of k and can take on any value greater than or equal to zero.

The first level is the nondegenerate ground state, $k = \ell = 0$, and the next three are degenerate states with $k = 0$, $\ell = 1$. We fill these states fully with eight electrons.

The next level is sixfold degenerate, with five d-orbital-like states with $k = 0$, $\ell = 2$, and an s-like state, with $k = 1$, $\ell = 0$. We place only two electrons, both of the same spin, in these six states. To preserve spherical symmetry, we equally occupy the d states with $2/7$ of an electron and place the remaining $4/7$ of an electron in the s state. Using the convention $\phi^m_{k\ell}$, the corresponding orbitals are

$$\phi^0_{10} = \left(\frac{\omega^3}{4\pi}\right)^{1/4}\left(\frac{3}{2} - \omega r^2\right)e^{-\frac{\omega}{2}r^2}, \tag{54}$$

$$\phi^m_{02} = \sqrt{\sqrt{\frac{\omega^3}{\pi}}\frac{2\omega^2}{15}}\, r^2 e^{-\frac{\omega}{2}r^2} Y^m_0. \tag{55}$$

In the limit that ω becomes infinite, there is no mixing between nondegenerate orbitals, so

$$\frac{\partial\rho}{\partial n^m_{k\ell}} = \phi^m_{k\ell}\phi^m_{k\ell} + 2\,\mathrm{Re}\sum_{\substack{k'\ell'm'\\ k''\ell''m''}} n_{k'\ell'}\mathbf{U}^{(1)m'',m'}_{k''\ell'',k'\ell'}\phi^{m'*}_{k'\ell'}\phi^{m''}_{k''\ell''}, \tag{56}$$

where the summations over k', ℓ', m' and k'', ℓ'', m'' have the appropriate limits so that $\phi^{m'}_{k'\ell'}$ and $\phi^{m''}_{k''\ell''}$ degenerate with $\phi^m_{k\ell}$.

The second derivative, or Hessian, of the total energy with respect to occupation numbers, then, simplifies to

$$\begin{aligned}\mathcal{H}_{n^m_{k\ell},n^{m'}_{k'\ell'}} &= \left\langle\phi^m_{k\ell}\middle|\frac{\delta v_{ks}}{\delta\rho}\phi^{m'}_{k'\ell'}\phi^{m'}_{k'\ell'}\middle|\phi^m_{k\ell}\right\rangle\\ &\quad + 2\,\mathrm{Re}\sum_{\substack{k''\ell''m''\\ jln}} n_{k''\ell''}\mathbf{U}^{\mu(1)m'',n}_{k''\ell'',jl}\left\langle\phi^m_{k\ell}\middle|\frac{\delta v_{ks}}{\delta\rho}\phi^{m''*}_{k''\ell''}\phi^n_{jl}\middle|\phi^m_{k\ell}\right\rangle,\end{aligned} \tag{57}$$

where the index μ refers collectively to k', ℓ', m'.

The constraint that the number of electrons is conserved decreases the dimension of the Hessian by one. Because we are only moving electrons between orbitals at the Fermi level, we can satisfy this constraint by setting

$$n_{1s} = 2 - \sum n^m_{k\ell}. \tag{58}$$

With this constraint, the Hessian becomes

$$\begin{aligned}\mathcal{H}_{n^m_{k\ell},n^{m'}_{k'\ell'}} &= \left\langle\phi^m_{k\ell}\middle|\frac{\delta v_{ks}}{\delta\rho}\phi^{m'}_{k'\ell'}\phi^{m'}_{k'\ell'}(1 - \delta_{k'\ell'm',100})\middle|\phi^m_{k\ell}\right\rangle\\ &\quad \times (1 - \delta_{k\ell m,100}) + 2\,\mathrm{Re}\sum_{\substack{k''\ell''m''\\ jln}} n_{k''\ell''}\mathbf{U}^{\mu(1)m'',n}_{k''\ell'',jl}\\ &\quad \times \left\langle\phi^m_{k\ell}\middle|\frac{\delta v_{ks}}{\delta\rho}\phi^{m''*}_{k''\ell''}\phi^n_{jl}(1 - \delta_{\mu,100})\middle|\phi^m_{k\ell}\right\rangle(1 - \delta_{k\ell m,100}).\end{aligned} \tag{59}$$

TABLE I. Eigenvalues of the Hessian of the total energy/$\sqrt{\omega}$ conserving the number of electrons.

No SIC	0.000	0.000	1.445	254.1	6969.5
With SIC	−100.2	−979.2	−951.0	−752.9	368.5

The eigenvalues of the constrained Hessian are given in Table I. In the first row, Slater's Xα functional [27,28] with $\alpha = 1$ was used for exchange without correlation.

The particular choice of XC potential does not affect the overall form of our equations and only determines the values of matrix elements that appear in various places. However, with $\alpha = 1$, the exchange interaction is not strong enough to favor integer occupation. All of the eigenvalues of the Hessian are either zero or positive, meaning that, to second order, the energy cannot be lowered by changing occupation numbers.

In the second row of Table I, we applied the self-interaction correction (SIC) of Perdew and Zunger [29] to Slater's exchange potential. Although the SIC is not well defined for fractionally occupied states, we can make a reasonable extension [13], where we use the following substitution:

$$\frac{\delta v_{ks}}{\delta\rho}\delta\rho|\phi_i\rangle \rightarrow \frac{\delta v_{ks}}{\delta\rho}(\delta\rho - \delta n_i\phi^*_i\phi_i - 2n_i\mathrm{Re}\phi^*_i\delta\phi_i)|\phi_i\rangle. \tag{60}$$

This correction eliminates the Coulomb and XC energy of any electron density in a given orbital with itself. Because the Coulomb energy is positive and typically much larger than the XC energy, the SIC will usually reduce the energy of integer occupied states relative to fractionally occupied states. This is apparent from the fact that, in the first row of Table I, four of the five eigenvalues are negative.

If the potential of the hole is expanded in multipole moments, because it consists only of negative charge which is symmetrically distributed around the center, and because the total charge of the hole doesn't change, the lowest-order term is its quadrupole moment. The change in potential then can be written as

$$\delta V \approx \frac{Q_{-2}Y^{-2}_2 + Q_{-1}Y^{-1}_2 + Q_0Y^0_2 + Q_1Y^1_2 + Q_2Y^2_2}{|\mathbf{r}|^3}. \tag{61}$$

The only term in this expression for δV with a diagonal matrix element in the d orbitals is Y^0_2, which corresponds to a stretch of the hole along the Z axis. To show that this corresponds to a zero eigenvector of Eq. (34), we note that, to pick out the Y^0_2 quadrupole, we must set $\mathbf{U}^{nm}_\ell = \delta_{m0}$. Multiplying this vector by the matrix in Eq. (34), we get

$$\sum_m\sum_{m'>m''}\left\langle\phi^{m''}_{k\ell}\middle|Y^q_2\middle|\phi^{m'}_{k\ell}\right\rangle\left\langle\phi^{m'}_{k\ell}\middle|Y^m_2\middle|\phi^{m''}_{k\ell}\right\rangle\delta_{m0} = 0, \tag{62}$$

because the matrix elements are only nonzero if $m + m'' - m' = 0$. Therefore, δ_{m0} is indeed a zero eigenvector.

The Z axis in particular is picked out by our choice of orbital basis. However, the spherical symmetry of the problem makes it equivalent to a stretch along any other axis. A different, symmetry equivalent direction could be picked out by rotating the orbitals into one another.

Note that after the hole is stretched along one direction it loses its spherical symmetry but retains axial symmetry. According to Jahn and Teller, this axially symmetric state is stable, which is apparent from our equations as well. The fact that only the Y_2^0 quadrupole has any diagonal matrix elements at the Fermi level means that, no matter how we shift the occupation numbers between these states, the molecule will remain stable along the X and Y axes.

For an elliptical charge distribution of charge q, radius R_0 along the X and Y axes, and a radius along the Z axis of $R_0 + \delta Z$, its quadrupole moment is

$$Q_2^0 = \frac{2q}{5}(2R_0\delta Z + \delta R^2), \tag{63}$$

and we have

$$\frac{\partial V(\mathbf{r})}{\partial Z} = \frac{4qR_0}{5|\mathbf{r}|^3}, \tag{64}$$

$$\frac{\partial^2 V(\mathbf{r})}{\partial Z^2} = \frac{4q}{5|\mathbf{r}|^3} = \frac{1}{R_0}\frac{\partial V(\mathbf{r})}{\partial Z}. \tag{65}$$

Because there are no discrete nuclei in this problem, the equivalent of the nuclear-nuclear interaction energy is potential energy of the positive jellium charge distribution. It can be computed from the electric field or, equivalently, the electrostatic potential, in atomic units as $(\nabla V)^2/8\pi$.

Only the second derivative of the nuclear-nuclear energy at $\delta Z = 0$ is needed to compute Jahn-Teller distortions, and we therefore only need to compute the term proportional to δZ^2, which is

$$\frac{4R_0^3 q^2}{50}\delta Z^2 \int_0^\pi \int_{R_0}^\infty \frac{9\left|Y_2^0\right|^2 + \frac{\partial}{\partial\theta}\left|Y_2^0\right|^2}{|\mathbf{r}|^6} \sin\theta \, d\mathbf{r}\, d\theta. \tag{66}$$

Substituting in the value of q from Eq. (52), we find

$$\frac{\partial^2 E_n}{\partial Z^2} = \frac{192}{5}\pi\omega^4 R_0^3. \tag{67}$$

The final piece we need to compute Jahn-Teller distortions, the derivative of the electron density with respect to occupation numbers, is obtained from PT. Because we are working in the limit that ω is infinite, the separation between energy levels is also infinite, and we can neglect occupied-virtual orbital mixing. The first-order density is then the result of the unitary transformations in Eqs. (25) and (26) that remove off-diagonal matrix elements between accidentally degenerate orbitals.

The spherical harmonic Y_2^0 couples only ϕ_{10}^0 and ϕ_{02}^0. Therefore, the first-order unitary matrices $\mathbf{U}^{n(1)}$ and $\mathbf{U}^{Z(1)}$ needed to decouple them have only a single nonzero element each. Plugging the relevant quantities into Eqs. (22) and (23), we get

$$\begin{aligned}\langle\phi_{10}^0|\frac{\partial V}{\partial Z}|\phi_{02}^0\rangle &= -\mathbf{U}_{02,10}^{Z(1)0,0}(n_{02} - n_{10}) \\ &\quad \times \langle\phi_{10}^0|\frac{\delta v_{ks}}{\delta\rho}\phi_{10}^0\phi_{02}^0|\phi_{02}^0\rangle,\end{aligned} \tag{68}$$

$$\begin{aligned}\langle\phi_{10}^0|\phi_{k\ell}^{*m}\phi_{k\ell}^m|\phi_{02}^0\rangle &= -\mathbf{U}_{02,10}^{n(1)0,0}(n_{02} - n_{10}) \\ &\quad \times\langle\phi_{10}^0|\frac{\delta v_{ks}}{\delta\rho}\phi_{10}^0\phi_{02}^0|\phi_{02}^0\rangle.\end{aligned} \tag{69}$$

TABLE II. Changes in energy and displacements associated with symmetry equivalent orbital occupations.

Occupied orbitals	With SIC		No SIC	
	$\delta E/\sqrt{\omega}$	$\delta Z \times 10^2\sqrt{\omega}$	$\delta E/\sqrt{\omega}$	$\delta Z \times 10^2\sqrt{\omega}$
$d^{\pm 2}d^{\pm 1}$	−1036.882	−1.194	352.187	0.308
$\mathbf{d^{\pm 2}d^0}$	−1076.244	−0.941	334.864	0.000
$d^{-2}d^2$	−800.650	−5.907	624.309	1.230
$d^{\pm 2}s$	−658.039	−2.765	260.406	0.615
$d^{\pm 1}d^0$	−899.188	3.771	497.271	−0.923
$d^{-1}d^1$	−962.790	3.518	407.767	−0.615
$\mathbf{d^{\pm 1}s}$	−687.870	1.947	206.271	−0.308
$d^0 s$	−657.626	2.200	261.129	−0.615

Equations (68) and (69) can be solved for $\mathbf{U}_{02,10}^{Z(1)00}$ and $\mathbf{U}_{02,10}^{n(1)00}$, which are used to generate $\partial\rho/\partial Z$ and $\partial\rho/\partial n_{k\ell}^m$ as

$$\begin{aligned}\frac{\partial\rho}{\partial Z} &= \mathbf{U}_{02,10}^{Z(1)00}\phi_{10}^0\phi_{02}^0 \\ &= -\frac{\langle\phi_{10}^0|\frac{\partial V}{\partial Z}|\phi_{02}^0\rangle\phi_{10}^0\phi_{02}^0}{(n_{02} - n_{10})\langle\phi_{10}^0|\frac{\delta v_{ks}}{\delta\rho}\phi_{10}^0\phi_{02}^0|\phi_{02}^0\rangle},\end{aligned} \tag{70}$$

$$\begin{aligned}\frac{\partial\rho}{\partial n_{k\ell}^m} &= \phi_{k\ell}^{*m}\phi_{k\ell}^m + \mathbf{U}_{02,10}^{n(1)00}\phi_{10}^0\phi_{02}^0 \\ &= -\frac{\langle\phi_{10}^0|\frac{\delta v_{ks}}{\delta\rho}\phi_{k\ell}^{*m}\phi_{k\ell}^m|\phi_{02}^0\rangle\phi_{10}^0\phi_{02}^0}{(n_{02} - n_{10})\langle\phi_{10}^0|\frac{\delta v_{ks}}{\delta\rho}\phi_{10}^0\phi_{02}^0|\phi_{02}^0\rangle} \\ &\quad + \phi_{k\ell}^{*m}\phi_{k\ell}^m.\end{aligned} \tag{71}$$

Putting everything together, we compute the stretch along the Z axis as

$$\begin{aligned}\delta Z &= \sum_{k\ell m}\frac{\partial Z}{\partial n_{k\ell}^m}\delta n_{k\ell}^m \\ &= \sum_{k\ell m}\frac{\int_{R_0}^\infty \frac{\partial\rho(\mathbf{r})}{\partial Z}\frac{4q}{|\mathbf{r}|^3}d\mathbf{r}\,\delta n_{k\ell}^m}{\int_{R_0}^\infty \frac{4q}{|\mathbf{r}^3|}\left(\frac{1}{R_0}\frac{\partial\rho(\mathbf{r})}{\partial Z} + \rho^{(0)}(\mathbf{r})\right)d\mathbf{r} + \frac{192\pi\omega^4}{5}R_0^2},\end{aligned} \tag{72}$$

where $\rho(\mathbf{r})$ is the original electron density, prior to shifting occupation numbers.

In Table II, we calculated δZ and the corresponding second-order change in energy for all fifteen possible integer occupation states, using $R_0 = 0.1/\sqrt{\omega}$. From these fifteen states, symmetry reduces the number of inequivalent energies and geometries to eight, because the resulting electron density is the same for $\phi_{k\ell}^m$ and $\phi_{k\ell}^{-m}$.

In the first column, the orbitals $\phi_{k\ell}^m$ are indicated with either s or d corresponding to an ℓ index of zero or 2, and a superscript indicating the m index. The index k is either zero or 1, as necessary so that $2k + \ell = 2$. In the first row, for example, there are four different combinations of occupied orbitals that are equivalent, where the first orbital is d-like with $m = \pm 2$ and $k = 0$, and the second orbital is also d-like with $m = \pm 1$ and $k = 0$.

With the self-interaction correction, all integer occupation states are lower in energy than the initial state, and the reverse is true without the self-interaction correction. In both cases, the lowest-energy integer-occupied state, calculated using the

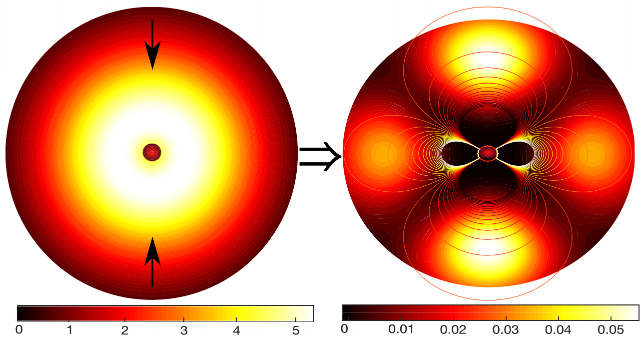

FIG. 1. Original electron density of the superatom per bohr^3 (left) and the change in density overlaid with the quadropole potential as it undergoes a Jahn-Teller distortion (right).

Hessian in Table I, is in bold, along with the accompanying δZ. Both states have a negative δZ corresponding to a shrink along the Z axis. The change in geometry and electron density for the calculation with a self-interaction correction is depicted in Fig. 1, with the compression along the Z axis exaggerated for visualization purposes.

V. CONCLUSIONS

Fractional occupation numbers can be used to give H_{KS} the same symmetries and degeneracies as the true quantum-mechanical Hamiltonian, which saves computational time in both the self-consistent field calculations and geometry optimizations. However, computing the true, Jahn-Teller distorted geometry requires moving electrons from a totally symmetric configuration into one that breaks symmetry. As electrons are shifted between orbitals, there is an associated shift in the ground-state geometry of the molecule.

Our equations determine the Jahn-Teller distortions, to second order, associated with moving electrons into a symmetry breaking configuration. Oftentimes, it will be desirable to move electrons into the lowest-energy state with integer occupation numbers, which we found for our example in Sec. IV using the Hessian of the energy with respect to occupation numbers.

Moving electrons between degenerate orbitals requires the use of degenerate PT, which is greatly simplified through exploitation of the molecule's point group. In the initial, symmetric configuration, there are multiple symmetry-equivalent choices of orbital basis as well as multiple symmetry-equivalent directions in which the molecule can distort. The particular choice of orbital basis picks out a corresponding subset of displacements from the symmetry adapted nuclear coordinates, which forms a basis for Jahn-Teller distortions.

This set of allowed nuclear displacements is chosen by the requirement that matrix elements of the resulting first-order nuclear potential vanish between degenerate orbitals from the same irrep. We then proved that this first-order nuclear potential generates first-order Coulomb and XC potentials in response that share the same symmetry properties. Matrix elements between degenerate orbitals from different irreps must by eliminated by a first-order unitary transformation that modifies the Coulomb and XC potentials in such a way that they cancel the off-diagonal elements of the nuclear potential.

Our method preserves the advantages of performing molecular calculations in the maximal symmetry and can be used for molecules of any size. The initial geometry optimization only needs to be carried out with respect to totally symmetric degrees of freedom, which are usually a small subset of all nuclear degrees of freedom, even in small but highly symmetric molecules. Symmetrizing the electron density also significantly reduces the number of degrees of freedom in the electronic wave function. The computational bottleneck of our method occurs in calculating derivatives of the electron density with respect to orbital occupations. However, only one such derivative is needed per degenerate orbital at the Fermi level, which does not necessarily grow larger with either the number of electrons or nuclei.

In our work, JT distortions can be understood as a consequence of symmetry breaking in the KS potential when integer occupation numbers are used. Perturbatively transforming a fractionally occupied solution into an integer occupied solution builds a connection between the original work of Jahn and Teller [1], which makes use of degenerate PT, and DFT, for which degenerate PT was only recently formulated [12–14].

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