

Rydberg atom arrays as quantum simulators for molecular dynamics

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Rydberg atoms held in optical tweezer arrays combine vibrational and electronic degrees of freedom that can be coupled and manipulated at a microscopic level. This opens opportunities for the quantum simulation of artificial molecular systems and offers in particular a platform for probing complex vibronic dynamics in controlled settings with increasing complexity. Tailored interatomic interactions and electron-phonon couplings yield handles for designing electronic state manifolds, for studying structural transitions, and for exploring non-classical vibrational states near molecular instabilities. Furthermore, this quantum simulator opens opportunities for testing and quantifying the validity of fundamental concepts, such as the Born-Oppenheimer approximation and quantum corrections to it.

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Introduction. Shedding light on dynamical processes within molecules is essential for many problems in physics, chemistry, and biology [1–4]. However, their coupled electronic and motional degrees of freedoms typically result in a high-dimensional state space that makes *ab initio* calculations forbiddingly complex [5]. This is particularly the case when common simplifications, such as the adiabatic approximation [6], for computing electronic potential surfaces are not applicable. An important example in this regard is the process of human vision that relies on a conformational change of molecular structure near crossing potential surfaces [7,8]. This and other related processes take place usually on an Angstrom length scale and on a femtosecond timescale. One approach to study them at directly observable length and drastically prolonged timescales—and thereby to shed light on their physics—is to use quantum simulators [9,10]. Initial steps into this direction have already been undertaken: Trapped ion setups have been used to mimic molecular dynamics near so-called conical intersections [11–13] and also recently for probing electronic state-dependent conformational changes in Wigner crystals [14]. Rydberg atoms have been employed to create macroscopically large Rydberg molecules [15–21], allowing to observe predissociation [22] and through strong continuum coupling emerging molecular states [23], as well as aggregates and clusters [24,25]. The latter were probed using the van der Waals explosion [26], in analogy to the Coulomb explosion [27], which is a means to infer molecular structure.

In this Letter, we showcase the potential of neutral atom arrays in optical tweezers [28–32] to serve as a quantum simulation platform for the study of molecular processes. To illustrate the capabilities of the simulator, we focus on three elementary molecular shapes of increasing complexity—a dumbbell, a triangle, and a tetrahedron. Already these simple examples reveal a range of intriguing properties, such as the emergence of motional instabilities and nonclassical, i.e., squeezed, vibrational ground states. The platform furthermore offers the capability of designing the structure of the electronic state space. More broadly, it allows to systematically investigate the impact of quantum effects, which become particularly important in regimes where the commonly used Born-Oppenheimer approximation (BOA) [6] breaks down. Rydberg tweezer arrays allow to quantitatively test the applicability of such approximations and to perform fully quantum mechanical investigations of molecular processes in system sizes that are intractable by exact numerical methods.

Molecular quantum simulator. We consider N optical tweezers, each confining a single atom [see examples in Figs. 1(a)–1(c)]. The dynamics of a single atom trapped in the k th tweezer is described by the single atom Hamiltonian ($\hbar \equiv 1$)

$$H^{(k)} = \Omega \sigma_x^{(k)} + \Delta n^{(k)} + \omega \sum_{j=x,y,z} (a_j^{(k)})^\dagger a_j^{(k)}. \quad (1)$$

The first two terms, with $\sigma_x = |\downarrow\rangle\langle\uparrow| + |\uparrow\rangle\langle\downarrow|$ and $n = |\uparrow\rangle\langle\uparrow|$, model a laser that drives transitions between the ground ($|\downarrow\rangle$) and Rydberg ($|\uparrow\rangle$) state with Rabi frequency Ω and detuning Δ [cf. Fig. 1(a)]. The second term describes the vibrations of the atom in the tweezer relative to its equilibrium position. Here, the phonon annihilation operators $a_j^{(k)}$ represent the corresponding displacements $\delta r_j^{(k)} = x_0(a_j^{(k)} + (a_j^{(k)})^\dagger)/\sqrt{2}$ in direction $j = x, y, z$ [see Fig. 1(c)], and $x_0 = 1/\sqrt{m\omega}$ is the harmonic oscillator length. For simplicity, we

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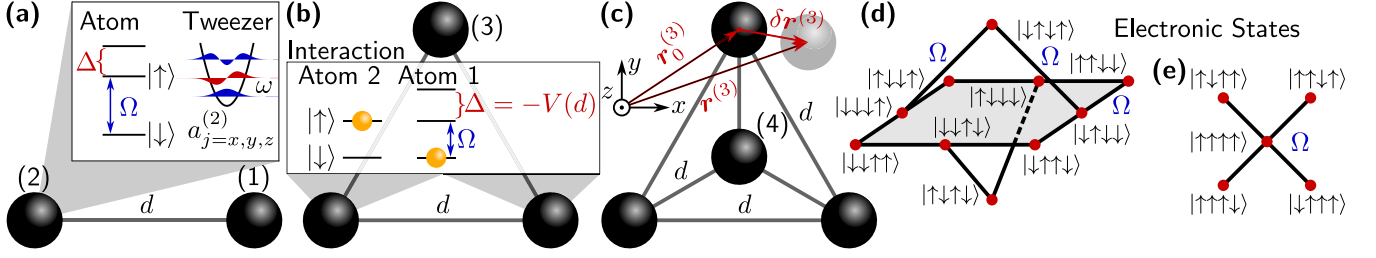


FIG. 1. Atom tweezer arrays and electronic state space. (a) Dumbbell-shaped atom array. Atoms are modeled by a two-level system with states $|\downarrow\rangle$ (ground state) and $|\uparrow\rangle$ (Rydberg state). Transitions are driven by a laser with detuning Δ and Rabi frequency Ω . The tweezer confinement is modeled by a harmonic oscillator with trapping frequency ω and phonon annihilation operators $a_j^{(k)}$ for the directions $j = x, y, z$. The superscript k labels the atom in the array. The atomic equilibrium positions of the dumbbell are $\mathbf{r}_0^{(1)} = d(1, 0, 0)^T$ and $\mathbf{r}_0^{(2)} = d(0, 0, 0)^T$. (b) Triangular atom array, obtained by extending the dumbbell with a third atom at position $\mathbf{r}_0^{(3)} = d(1/2, \sqrt{3}/2, 0)^T$. If atom 2 is in its Rydberg state, the Rydberg state of atom 1 experiences the interaction energy shift $V(d)$. When the laser detuning cancels this interaction shift, $\Delta = -V(d)$, atom 1 undergoes a facilitated excitation. (c) Tetrahedral atom array, obtained from the triangle [see panel (b)] by adding an atom at position $\mathbf{r}_0^{(4)} = d(1/2, 1/(2\sqrt{3}), \sqrt{2}/3)^T$. The position $\mathbf{r}^{(k)} = \mathbf{r}_0^{(k)} + \delta\mathbf{r}^{(k)}$ of the k th atom in the array is the sum of the equilibrium position $\mathbf{r}_0^{(k)}$ and the displacement vector $\delta\mathbf{r}^{(k)}$, with components $\delta r_j^{(k)} = x_0(a_j^{(k)} + (a_j^{(k)})^\dagger)/\sqrt{2}$. (d), (e) Visualization of coupled (at rate Ω) resonant electronic states of the tetrahedron. The graph in panel (d) emerges when choosing the facilitation condition $\Delta = -V(d)$, and panel (e) is obtained when setting $\Delta = -3V(d)$.

assume the tweezer potentials to be isotropic and electronic state independent [33,34]. The full many-body Hamiltonian of the tweezer array is

$$H = \sum_{k=1}^N H^{(k)} + \sum_{k=1}^N \sum_{l=1}^{k-1} V(r^{(k,l)}) n^{(k)} n^{(l)}, \quad (2)$$

where $V(r^{(k,l)})$ describes interactions between Rydberg atoms as a function of the distance $r^{(k,l)}$ between the k th and l th atom. Typically, the interaction potential follows a power law [35–37]. However, using Förster resonances and external optical and microwave fields allows one to create a variety of shapes [38–42], including Lennard-Jones-type potentials with repulsive core and attractive long-range tail. Typical atom equilibrium distances in tweezer arrays are $d \approx 3\text{--}6\text{ }\mu\text{m}$ [43–45] and trap frequencies can be on the order of $\omega = 100\text{ kHz} \approx 2\pi \times 16\text{ kHz}$. For ^7Li atoms, this yields a harmonic oscillator length of $x_0 = 1/\sqrt{\omega m} \approx 300\text{ nm}$ and hence a ratio between atomic displacement and interatomic separation of $v = x_0/d \lesssim 0.1$. Close to the vibrational ground state, this justifies the following expansion of the interaction potential:

$$V(r^{(k,l)}) \approx V(r_0^{(k,l)}) + \mathbf{G}^{(k,l)} \delta\mathbf{r}^{(k,l)} + \frac{1}{2} (\delta\mathbf{r}^{(k,l)})^T (H_a^{(k,l)} + H_b^{(k,l)}) \delta\mathbf{r}^{(k,l)}, \quad (3)$$

with $\delta\mathbf{r}^{(k,l)} = \delta\mathbf{r}^{(k)} - \delta\mathbf{r}^{(l)}$. Here, the second and third term couple the electronic state-dependent interaction to the vibrations of the atoms inside the tweezer potential [46]. The strength and nature of this vibronic coupling are quantified by the expansion coefficients

$$\mathbf{G}^{(k,l)} = V'(r_0^{(k,l)}) \frac{(\mathbf{r}_0^{(k,l)})^T}{r_0^{(k,l)}}, \quad (4)$$

$$H_a^{(k,l)} = V''(r_0^{(k,l)}) \frac{\mathbf{r}_0^{(k,l)}}{r_0^{(k,l)}} \otimes \frac{(\mathbf{r}_0^{(k,l)})^T}{r_0^{(k,l)}}, \quad (5)$$

$$H_b^{(k,l)} = \frac{V'(r_0^{(k,l)})}{r_0^{(k,l)}} \left[1_3 - \frac{\mathbf{r}_0^{(k,l)}}{r_0^{(k,l)}} \otimes \frac{(\mathbf{r}_0^{(k,l)})^T}{r_0^{(k,l)}} \right], \quad (6)$$

where $\mathbf{r}_0^{(k,l)} = \mathbf{r}_0^{(k)} - \mathbf{r}_0^{(l)}$ denotes the distance vector between equilibrium positions and $r_0^{(k,l)} = \|\mathbf{r}_0^{(k,l)}\|$. The gradient $\mathbf{G}^{(k,l)}$ and Hessian $H_a^{(k,l)} + H_b^{(k,l)}$ lead to linear and quadratic vibronic coupling [see Eqs. (2) and (3)], respectively.

Molecular Hamiltonians. To get a first impression of the capabilities of the simulator, we first focus on the dumbbell depicted in Fig. 1(a). In order to simplify the problem, we employ the facilitation condition $\Delta = -V(d)$ and $|\Delta| \gg |\Omega|$ [47–52] [see Fig. 1(b)]. This splits the electronic Hilbert space into two approximately decoupled [53] manifolds of resonant states: $\{|\downarrow\downarrow\rangle\}$ and $\{|\downarrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\uparrow\uparrow\rangle\}$, with energy separation $|\Delta|$. Only the latter one features vibronic couplings. Here, the constrained [54–56] electronic dynamics can be represented by a tight-binding model on a graph, where Ω is the coherent hopping rate between nodes: $|\downarrow\uparrow\rangle \xleftrightarrow{\Omega} |\uparrow\uparrow\rangle \xleftrightarrow{\Omega} |\uparrow\downarrow\rangle$. In fact, a further simplification is achieved by introducing the state $|+\rangle = (|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle)/\sqrt{2}$, which restricts the electronic dynamics to the space $\{|+\rangle, |\uparrow\uparrow\rangle\}$. Furthermore, introducing the vibrational mode of the relative motion, $b = (a^{(1)} - a^{(2)})/\sqrt{2}$, yields the following compact matrix representation of the dumbbell Hamiltonian:

$$H_2 = \begin{bmatrix} \omega b^\dagger b & \sqrt{2}\Omega \\ \sqrt{2}\Omega & \omega b^\dagger b + \sqrt{2}\kappa(b + b^\dagger) + \xi(b + b^\dagger)^2 \end{bmatrix}. \quad (7)$$

Here, we defined the vibronic coupling constants $\kappa = x_0 V'(d)/\sqrt{2}$ and $\xi = x_0^2 V''(d)/2$, which depend on the interaction potential gradient and curvature at the interatomic equilibrium distance d . This Hamiltonian illustrates the general idea behind the quantum simulator of molecular phenomena: Diagonal entries describe the motion of “nuclear” degrees of freedom in electronic potential energy surfaces, which are a combination of the tweezer trap and the state-dependent interaction potential. These surfaces are hybridized by the off-diagonal entries due to the laser coupling with Rabi

frequency Ω . In general, the shape of the Hamiltonian can thus be engineered by controlling the Rydberg interaction potential V , i.e., through κ and ξ , the structure of the electronic state space, and the geometric arrangement of the tweezers. To illustrate this further, we consider next the tetrahedron depicted in Fig. 1(c). More atoms yield a larger electronic Hilbert space and choosing the laser detuning Δ allows to engineer different graphs of resonant electronic states: setting $\Delta = -V(d)$ yields the multiple-connected graph in Fig. 1(d) and setting $\Delta = -3V(d)$ leads to the star graph shown in Fig. 1(e). Generally, the emerging vibronic Hamiltonians take the form

$$H_{\text{mol}} = \Omega \sum_{ss'} A_{ss'} |s\rangle \langle s'| + \sum_s h_s |s\rangle \langle s|, \quad (8)$$

where the matrix A is the adjacency matrix of the graph representing the electronic states that are resonantly connected by the laser. Furthermore, the Hamiltonians h_s model the electronic state-dependent vibrational “nuclear” dynamics. For the particular case of the tetrahedron and the graph in Fig. 1(d), A is ten dimensional and the indices s and s' run over all electronic states contained in the graph. In states containing one Rydberg excitation, vibrations are solely governed by the tweezer confinement: $h_s = \omega b_s^\dagger b_s$, where we collected all modes in the vector b_s . States containing two Rydberg atoms feature a significantly more complex vibrational dynamics, which is governed by

$$h_s = \omega b_s^\dagger b_s + \sqrt{2}\kappa(b_s^\parallel + (b_s^\parallel)^\dagger) + \xi(b_s^\parallel + (b_s^\parallel)^\dagger)^2 + \frac{\nu\kappa}{\sqrt{2}}(b_s^{\perp,1} + (b_s^{\perp,1})^\dagger)^2 + \frac{\nu\kappa}{\sqrt{2}}(b_s^{\perp,2} + (b_s^{\perp,2})^\dagger)^2. \quad (9)$$

The parallel modes describe displacements along the tetrahedron’s edges, analogously to b in Eq. (7). The perpendicular modes govern motion within the plane perpendicular to each edge. For details, see the Supplemental Material [57].

Molecular instabilities and ground-state squeezing. Let us now discuss some phenomena that can be explored with the quantum simulator. To this end, we return to the dumbbell in Eq. (7) and consider the limit $\Omega \rightarrow 0$. Here, the Hamiltonian can be diagonalized by a state-dependent Bogoliubov transformation (BT). In the $|+\rangle$ state this is trivial, whereas in the $|\uparrow\uparrow\rangle$ state we have the transformed mode (see the supplemental Material [57]) $b_{\text{BT}} = (b + wb^\dagger)/\sqrt{1-w^2}$, where

$$w = 1 + \phi - \frac{\phi}{|\phi|} \sqrt{(1+\phi)^2 - 1}, \quad \phi = \frac{\omega}{2\xi}. \quad (10)$$

Crucially, w exists only if $\xi > \xi_c$, where $\xi_c = -\omega/4$ is the critical potential curvature. Outside this regime, the electron-phonon coupling renders the system unstable. This becomes also apparent from the molecular ground-state energy (MGSE), which for $\Omega = 0$ reads $E_{\text{GS},2} = \min\{\omega\varepsilon_2, 0\}$, with

$$\varepsilon_2 = -\frac{2\kappa^2}{\omega^2} \frac{1}{1-\bar{\xi}} + \frac{1}{2} \sqrt{1-\bar{\xi}} - \frac{1}{2}, \quad \bar{\xi} = \frac{\xi}{\xi_c}. \quad (11)$$

At $\xi = \xi_c$, the denominator of the first term vanishes and the energy diverges. For finite Ω , we computed the MGSE numerically, which is shown as the blue curve in Figs. 2(a) and 2(b). Clearly, the ground-state energy is lowered as $|\xi - \xi_c|$

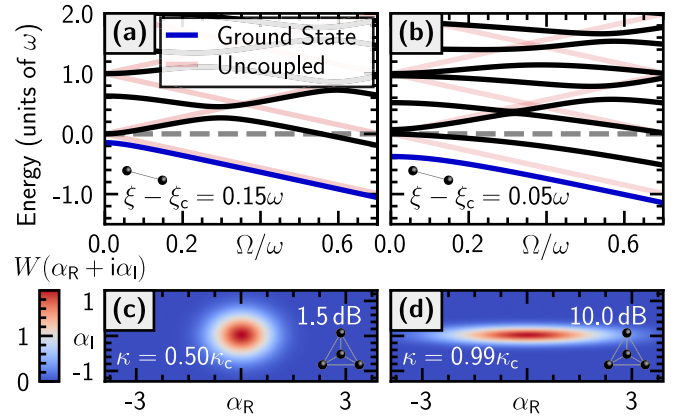


FIG. 2. Energy spectrum and Wigner distribution. (a), (b) Energy spectrum (black) of the dumbbell [Fig. 1(a)] as a function of the Rabi frequency Ω . The spectrum is computed by exact diagonalization of Eq. (7) with $\kappa = 0.1\omega$ and truncating at 100 phonons. In blue, we highlight the ground state. As a reference, we show the uncoupled ($\kappa = \xi = 0$) spectrum (red). (c), (d) Wigner quasiprobability distribution of the ground state of the tetrahedron [Fig. 1(c)] and Eq. (13), for different values of κ . We choose $\xi = 2\omega$ and $\nu = 0.1$. In the top right, the squeezing strengths (variance of the position quadrature associated with the mode with annihilation operator $b_{|\uparrow\uparrow\downarrow\downarrow}^{\perp,1}$) normalized to the variance for $\kappa = \xi = 0$) are shown.

decreases and achieving numerical convergence becomes increasingly difficult as the instability is approached. In fact, the instability at ξ_c is expected to occur for arbitrary Rabi frequencies Ω because Eq. (10) does not depend on Ω . Physically, we understand the instability at ξ_c as the consequence of the trapping potential being canceled by the quadratic perturbations of the harmonic oscillator in Eq. (7). This is a somewhat trivial effect. The tetrahedron, on the other hand, features a second, in fact more interesting, instability that we find upon inspection of its ground-state energy (at $\Omega = 0$). It is given by $E_{\text{GS},4} = \min\{\omega\varepsilon_4, 0\}$, with

$$\varepsilon_4 = -\frac{2\kappa^2}{\omega^2} \frac{1}{1-\bar{\xi}} + \frac{1}{2} \sqrt{1-\bar{\xi}} + \sqrt{1-\bar{\kappa}} - \frac{3}{2}, \quad \bar{\kappa} = \frac{\kappa}{\kappa_c}. \quad (12)$$

This expression is obtained by employing the BT defined by Eq. (10) to the Hamiltonians h_s in the state space contained in the graph of Fig. 1(d). A direct inspection shows that, in addition to the instability at ξ_c , we obtain a second one at $\kappa_c = -\omega/(2\sqrt{2}\nu)$, manifesting in an imaginary square root when $\kappa < \kappa_c$. This second instability can be characterized through the squeezing of the ground-state wave function: For $\Omega = 0$, a ground state of Eq. (8) is the product $|\uparrow\uparrow\downarrow\downarrow\rangle \otimes |\text{GS}\rangle$, where $|\text{GS}\rangle$ is the ground state of $h_{|\uparrow\uparrow\downarrow\downarrow}$ defined in Eq. (9). Its Wigner quasi-probability distribution for the mode $b_{|\uparrow\uparrow\downarrow\downarrow}^{\perp,1}$ is, with $\alpha = \alpha_R + i\alpha_I$,

$$W(\alpha) = \frac{2}{\pi} \exp(-\bar{w}_+ \alpha_R^2 - \bar{w}_- \alpha_I^2), \quad \bar{w}_{\pm} = 2 \frac{1 \pm w}{1 \mp w}, \quad (13)$$

as is derived in the Supplemental Material [57]. We plot this function for different values of κ in Figs. 2(c) and 2(d), to show the increasingly squeezed shape for $\kappa \searrow \kappa_c$

when approaching the instability. Importantly, although we are close to the critical point, $\kappa = 0.99\kappa_c$, where one could expect large ground-state displacements because of weak atom confinement, the atoms are in fact on average closer than $0.4x_0$ to their equilibrium positions (see the Supplemental Material [57]). We note here that going beyond the considered limit, $\Omega = 0$, requires exact numerical diagonalization. This is, however, rather challenging, given that already for such a small system—with all symmetries considered—nine vibrational modes and ten electronic states [see Fig. 1(d)] are involved. We also note that our treatment does not consider the mechanical recoil energy transferred to the atom by the laser excitation. This is typically justified when the atoms are tightly confined and the corresponding Lamb-Dicke parameter is small (see, e.g., Ref. [59]). However, close to the unstable regime, the system features collective vibrational modes with low vibration frequency. This is likely to quantitatively alter the results, such as the location of the critical point κ_c . We will investigate this in the future.

Structural molecular transitions. Finally, let us show that this quantum simulation platform permits the investigation of structural molecular transitions and allows to study the impact of quantum effects on those. To this end, we consider the triangle shown in Fig. 1(b), which can undergo a transition from a symmetric to a symmetry-broken ground state. Employing the facilitation condition, $\Delta = -V(d)$, its resonant electronic subspace is spanned by the states $\{|\downarrow\downarrow\uparrow\rangle, |\downarrow\uparrow\downarrow\rangle, |\downarrow\uparrow\uparrow\rangle, |\uparrow\downarrow\downarrow\rangle, |\uparrow\downarrow\uparrow\rangle, |\uparrow\uparrow\downarrow\rangle\}$. The resulting Hamiltonian has the structure of Eq. (8) with $b_s^{\perp,2} = 0$ and an adjacency matrix that describes a ring-shaped graph [60]. To see the structural transition, it is sufficient to employ the so-called BOA, which amounts to neglecting the kinetic energy of the “nuclei.” The resulting Born-Oppenheimer potential energy surfaces (BOPESSs) depend on four collective coordinates (bosonic modes), which we label q_i , $i = 1, 2, 3, 4$ (see the Supplemental Material [57]). To compute the MGSE, we minimize the (classical) BOPES $E_{\text{BO}}(\Omega; \mathbf{q})$, defined as the smallest eigenvalue of the Hamiltonian for a fixed position $\mathbf{q} = (q_1, q_2, q_3, q_4)^T$ and Rabi frequency Ω . Note that for $\Omega = 0$, there are three degenerate ground states [60], one for each nonsymmetric triangular shape in the top right of Fig. 3(a). This is the so-called Jahn-Teller effect [60–62]. In the vicinity of the leftmost symmetry-broken triangle, and for $\Omega = 0$, the BOPES reads

$$E_{\text{BO}}(0; \mathbf{q}) = \frac{\omega}{2x_0^2} \mathbf{q}^2 + \frac{2\kappa}{x_0} q_{\parallel} + \frac{2\xi}{x_0^2} q_{\parallel}^2 + \frac{\sqrt{2}\nu\kappa}{x_0^2} q_{\perp}^2, \quad (14)$$

where $q_{\parallel} = (q_1 - q_2)/\sqrt{2}$ and $q_{\perp} = (q_3 + q_4)/\sqrt{2}$.

Increasing the Rabi frequency leads to a change of the molecular configuration: the distorted triangle becomes a symmetric one [see Fig. 3(a)]. This structural transition is reflected in the ground-state energy, which is shown in Fig. 3(b), where we display both the full quantum mechanical result (blue) and the BOA (red). The BOA shows a kink at the transition point, whereas the full numerical calculation yields a smooth curve and is also shifted. These discrepancies are quantum corrections, which are not accounted for by the BOA. The relative shift can be computed analytically for

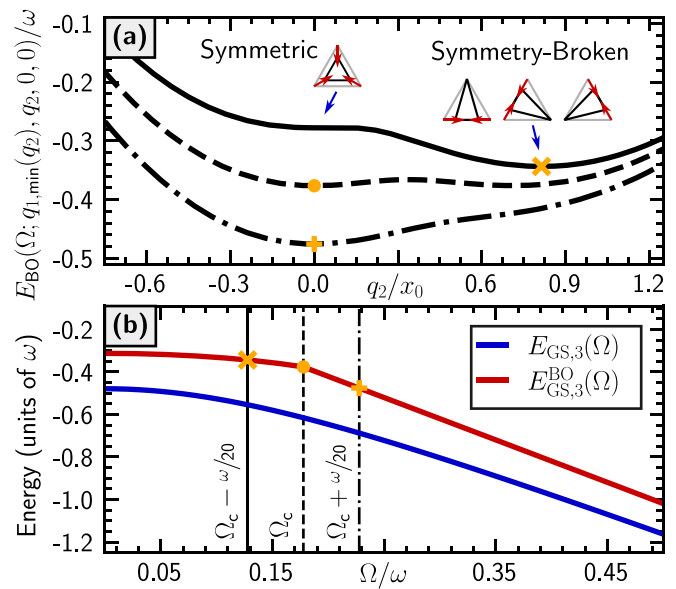


FIG. 3. Potential energy surfaces and ground-state energy. (a) Ground-state potential energy surface for the triangle shown in Fig. 1(b). We plot the surface in the vicinity of one of the threefold degenerate minima: the one that is associated with configurations in the vicinity of the leftmost of the three deformed triangular shapes. For $\Omega = 0$, this surface is given by Eq. (14). The curves shown here are $E_{\text{BO}}(\Omega; q_{1,\min}(q_2), q_2, q_3 = 0, q_4 = 0)$, and the minimum of each curve (see yellow markers) corresponds to the ground state within the BOA for a given Ω . At $\Omega = \Omega_c$, a structural transition between a symmetric and a symmetry-broken triangle takes place (dashed line). For details, see the Supplemental Material [57]. For the electron-phonon coupling parameters, we chose $\xi = -0.15\omega$, $\kappa = 0.25\omega$, and $\nu = 0.1$. (b) Ground-state energy of the triangle as a function of the Rabi frequency Ω . The curve $E_{\text{GS},3}(\Omega)$ (blue) is obtained by exact diagonalization (truncated at 20 phonons per mode). The red curve shows the ground-state energy $E_{\text{GS},3}^{\text{BO}}(\Omega)$, obtained in the BOA.

$\Omega = 0$,

$$E_{\text{GS},3} - E_{\text{GS},3}^{\text{BO}} = \frac{\omega}{2} \left[\sqrt{1 - \xi} + \sqrt{1 - \kappa} - 2 \right], \quad (15)$$

and the explicit calculation (see the Supplemental Material [57]) indeed shows that a nonvanishing commutator between bosonic operators is its origin. The observed smoothed transition is a consequence of the fact that in the vicinity of the transition it is not sufficient to merely consider the minima of the BOA to compute the ground-state energy. In fact, here the formerly neglected kinetic energy leads to tunneling between the minima and a gradual and smooth change of the ground-state energy. Let us now briefly discuss how to observe the symmetry-broken regime and the concomitant structural transition experimentally. One possibility is to measure the atoms' vibrational Wigner function as outlined in Refs. [63,64]. Moreover, one can infer their real-space probability distribution by field ionizing the atoms and subsequently detecting them with high-resolution ion microscopes (see Ref. [65]). Furthermore, as we show in the Supplemental Material [57], it is possible to observe signatures of the symmetry-broken regime and concomitant structural transition on the basis of

Rydberg density measurements, i.e., without even probing the vibrational degrees of freedom.

Summary and conclusions. Optical tweezer arrays in conjunction with Rydberg excitations offer new opportunities for engineering many-body systems that share central features of complex molecules. Already the simple examples discussed in this work showcase a whole host of interesting phenomena. The quantum simulation toolbox can be further enhanced by introducing resonant (and orientation-dependent) dipolar interactions, which yield a further mechanism—in addition to facilitation—for electronic excitation hopping. This may allow to engineer more complex molecular potential landscapes, for example, conical intersections [11]. Further handles to enrich the quantum simulator are state-dependent and anisotropic tweezer potentials. Ultimately, such a quantum simulator may allow to address fundamental questions concerning dynamical processes in extended molecules. Examples include the impact of vibronic coupling on excitation transfer [66] in light harvesting complexes [67]. Such

systems are notoriously difficult to model as the number of phonon degrees of freedom is too large to be exactly simulated [68]. Yet, it is too small to be effectively accounted for through a simple unstructured bath, which would enable a master equation description [69].

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Data availability. The data that support the findings of this article are openly available [70].

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