

Trap-assisted creation of giant molecules and Rydberg-mediated coherent charge transfer in a Penning trap

I. Lesanovsky, M. Müller, and P. Zoller

Institute for Theoretical Physics, University of Innsbruck, and Institute for Quantum Optics and Quantum Information of the Austrian Academy of Sciences, Innsbruck, Austria

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We study two ions confined in a Penning trap. We show that electronically highly excited states exist in which an electron is delocalized among the two ions forming a giant molecule of several micrometer size. At energies close to the top of the Coulomb barrier, these molecular states can be regarded as superpositions of Rydberg states of individual ions. We illuminate the possibility to observe coherent charge transfer between the ions. Beyond a critical principal quantum number, the electron can coherently tunnel through the Coulomb barrier to an adjacent doubly charged ion. The tunneling occurs on time scales on which the dynamics of the nuclei can be considered frozen and radiative decay can be neglected. The present study can be regarded as a first step toward the implementation of electronic Hubbard models in an ion-trap setup.

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As the simplest conceivable molecule, singly ionized molecular hydrogen H_2^+ is formed out of two protons and a single delocalized electron tying the protons together with an equilibrium distance of just a few Bohr's radii (a_0). In 2000, Greene *et al.* complemented this class of conventional homonuclear binary molecules by predicting a new type of ultralong-range molecules [1] in which a Rydberg atom forms a molecular entity with a ground-state atom. Recently, such molecular states, where the electron is delocalized over two nuclei which are separated by 1000 or more a_0 , have been observed experimentally [2]. Moreover, it has been shown that Rydberg atoms can form molecular states even if their electronic wave functions do not overlap [3–5]. The atoms are held together by the multipole interaction of their charge distributions, giving rise to equilibrium distances of again several thousand a_0 . Another class of “molecular species,” which, however, can only exist in a trap, is constituted by trapped ions [6,7]. At sufficiently low temperatures the mutual Coulomb repulsion, which is compensated by the trapping potential leads to the formation of a Wigner crystal with the interparticle spacing being typically of the order of μm . The ions can be cooled to their motional ground state such that the low-energy excitations are small oscillations around their equilibrium positions. These phonons are reminiscent of vibrational molecular excitations. However, unlike for the previously mentioned molecular species, there are no delocalized electrons in this system.

In this work we show theoretically the possibility to create *delocalized electronic states* among positively charged ions separated by several micrometers and confined in a Penning trap [6,8], which by itself does not provide confinement for negatively charged particles. However, delocalized bound electronic states of *micrometer size* are shown to exist, forming a new class of trap-induced quantum objects. We study the case of two ions, one singly and the other one doubly charged. This situation is reminiscent of the H_2^+ molecule, but with the difference that in the present setup the internuclear distance can be controlled by the trapping fields and the “nuclei” are individually addressable by lasers. In particular, we investigate states whose energy lies just below the Cou-

lomb barrier separating the ionic charges. Such states can be thought of as being a superposition of states in which a single electron occupies a Rydberg state that can be associated with an individual ion. Along this line we study coherent charge transfer—i.e., the process $A^{++}+A^+ \rightarrow A^++A^+$ —which can be understood as coherent tunneling of a laser-excited electron between Coulomb wells. We find tunneling rates of the order of hundreds of MHz. On the corresponding time scale the ionic motion can be considered frozen and radiative decay plays no role. We discuss the dynamics of the charge transfer, showing that quantum-mechanical superpositions of two macroscopic dipole moments (configurations $A^{++}+A^+$ and A^++A^+) differing by 10^5 D can be created. The resulting change in the electric field can be employed to coherently control other quantum-mechanical systems over large distances. Moreover, our work represents a first step toward the implementation of tight-binding or Hubbard models for electrons in an ion trap. Compared to implementations relying on atoms in optical lattices, the corresponding tunneling rates are increased by up to six orders of magnitude.

The Penning trap is constituted by a homogeneous magnetic field $\mathbf{B} = B\mathbf{e}_z$ of strength B and an electric quadrupole field with the potential $\Phi(\mathbf{r}) = -\beta[x^2 + y^2 - 2z^2]$, with β being the field gradient. In the symmetric gauge, the vector potential is $\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times \mathbf{r}$ and the motion of a particle of charge Qe and mass M in this trap is governed by the Hamiltonian [8]

$$\begin{aligned} H(\mathbf{p}, \mathbf{r}; Q, M) &= \frac{1}{2M} [\mathbf{p} - Qe\mathbf{A}(\mathbf{r})]^2 + Qe\Phi(\mathbf{r}) \\ &= \frac{\mathbf{p}^2}{2M} - \frac{\omega_c}{2} L_z + \frac{1}{2} M [\omega_\rho^2 \rho^2 + \omega_z^2 z^2]. \end{aligned} \quad (1)$$

Here $L_z = xp_y - yp_x = -i\hbar\partial_\phi$ is the z component of the total angular momentum and we have introduced the radial $\omega_\rho = \sqrt{(2/M)[(Qe)^2 B^2 / (8M) - Qe\beta]}$ and longitudinal $\omega_z = 2\sqrt{(Qe\beta)/M}$ trap frequencies as well as the cyclotron frequency $\omega_c = (QeB)/M$. In order to provide radial confinement, ω_ρ has to be real, which is achieved beyond the critical

field strength $B_1 = \sqrt{(8M\beta)/(Qe)}$. We intend to operate the Penning trap in a regime where $\omega_\rho > \omega_z$, thus forming a prolate trap [9].

We focus on a scenario with two ions being of the same atomic species, but carrying different charges. The feasibility of preparing and cooling two ion systems in a Penning trap has been experimentally demonstrated in Ref. [9]. The Hamiltonian for *two ions in their electronic ground state*, where they can be described by two point charges, reads

$$H_g = H(\mathbf{P}_1, \mathbf{R}_1; Q_1, M) + H(\mathbf{P}_2, \mathbf{R}_2; Q_2, M) \\ + V_C(|\mathbf{R}_1 - \mathbf{R}_2|; Q_1, Q_2),$$

with the Coulomb interaction $V_C(|\mathbf{R}_1 - \mathbf{R}_2|; Q_1, Q_2) = (Q_1 Q_2 e^2)/(4\pi\epsilon_0 |\mathbf{R}_1 - \mathbf{R}_2|)$. We assume that the ionic motion has been cooled to the ground state such that the ions perform harmonic oscillations around their equilibrium positions:

$$\mathbf{R}_{0,k} = \frac{\zeta}{2} \left(0, 0, \frac{(1-k)Q_1 + (2-k)Q_2}{(Q_1 + Q_2)^{2/3}} \right), \quad (2)$$

with the characteristic length $\zeta = [e/(2\pi\epsilon_0\beta)]^{1/3}$ and $k=1, 2$. The transverse oscillation frequencies are given by the respective values of ω_ρ , whereas the frequencies of the longitudinal modes evaluate to $\omega_{z,\pm}^2 = (2e\beta)/[M(Q_1 + Q_2)](Q_1^2 + 6Q_1Q_2 + Q_2^2 \pm \sqrt{Q_1^4 + 14Q_1^2Q_2^2 + Q_2^4})$. Throughout this work we will consider ^{40}Ca with $Q_1=2$ and $Q_2=1$ confined to a Penning trap with the parameters $B=10$ T and $\beta=2 \times 10^6$ V/m². In this case we find $\omega_{\rho,1}=2\pi \times 3.78$ MHz, $\omega_{\rho,2}=2\pi \times 1.85$ MHz, $\omega_{z,-}=2\pi \times 0.83$ MHz, and $\omega_{z,+}=2\pi \times 1.44$ MHz. We furthermore have $\zeta=11.29$ μm and consequently an interionic distance of $D=8.14$ $\mu\text{m}=153 \times 10^3 a_0$, which allows for individual laser addressability.

The idea of creating delocalized electronic states in this setup is as follows: The valence electron of the singly charged ion is excited by a laser to a high-lying electronic (Rydberg) state. Here the electron is exposed to the potential of *two doubly charged ions*. The electron can hop as soon as its wave function overlaps with the empty Rydberg orbital of the second ion. By this, electronic states that extend over both ionic cores are formed and the electronic charge can be transferred. The size of a Rydberg orbit is approximately given by $r_{\text{Ryd}}=(2a_0n^2)/Q$, with n being the principal quantum number. Requiring r_{Ryd} to be half the equilibrium distance D between the ions one finds that delocalized electronic states are expected to occur beyond $n > n_{\text{ct}} = \sqrt{D/(2a_0)} \approx 277$ for the above parameters. Indeed, we will see later that this is the case even for much smaller values of n .

In order to study the process more quantitatively, we consider the electronic Hamiltonian

$$H_{\text{el}} = H(\mathbf{p}, \mathbf{r}; -1, m) + V_C(|\mathbf{r} - \mathbf{R}_{0,1}|; 2, -1) \\ + V_C(|\mathbf{r} - \mathbf{R}_{0,2}|; 2, -1), \quad (3)$$

where m denotes the electron mass and the ions are frozen at their equilibrium position. The electronic spin is not considered as it merely gives rise to a constant energy offset. In Eq. (3) we have approximated the interaction potential between

the ionic cores and the electron by a sum of two pure Coulomb potentials of charge $2e$. This is a simplification, since in general the true potential will deviate from the Coulomb potential at small distances due to the presence of the inner electronic shells. For Rydberg states this gives rise to the quantum defect of states with low angular momenta [10]. The general features of the charge transfer, however, will not be affected by the actual value of the quantum defect and an experimental implementation requires in any case a careful spectroscopic analysis.

In the following, we will motivate an adiabatic single-channel approximation in order to derive an effective one-dimensional electronic Hamiltonian. To this end it is instructive to consider the part of $H(\mathbf{p}, \mathbf{r}; -1, m)$ in Eq. (3), which governs the transverse electronic dynamics, providing harmonic confinement with the frequency $\Omega_\rho = \sqrt{(2/m)[(e^2B^2)/(8m) + e\beta]} = 2\pi \times 140$ GHz. The eigenstates of this potential are given by the two-dimensional harmonic oscillator states $\Theta_{\nu,\mu}(\rho, \phi)$ with the energies $E_{\nu,\mu} = \hbar(\Omega_c/2)\mu + \hbar\Omega_\rho(2\nu + |\mu| + 1)$, where $\Omega_c = (eB)/m$. We will see *a posteriori* that in the regime of interest the energy gap between the states $\Theta_{\nu,\mu}(\rho, \phi)$ and $\Theta_{\nu\pm 1,\mu}(\rho, \phi)$ is much larger than the energy of the longitudinal electronic motion. Therefore we can neglect the coupling between oscillator states with different ν . For fixed ν , states with different μ are only coupled if the interatomic axis does not coincide with the z axis. For infinitely heavy ions in equilibrium, this is not the case. In the case of finite mass, the corresponding couplings will lead to a modification of the electronic wave function depending on the positions of the ions, which has to be taken into account by averaging over the ionic probability density. The dominant part of this averaging, however, will arise from the configuration where both ions are located on the z axis. We therefore can neglect couplings between states with different μ and still obtain a qualitatively correct picture. In our approximation the transversal electronic motion is frozen in the oscillator ground state $\Theta_{0,0}(\rho, \phi) = (\sqrt{\pi}\rho_0)^{-1} \exp[-(\rho/\rho_0)^2/2]$, with $\rho_0 = \sqrt{\hbar/(m\Omega_\rho)} \approx 216a_0$, and we use the ansatz $\Psi(\rho, z, \phi) = \Theta_{0,0}(\rho, \phi)\phi(z)$ for the electronic eigenstates. Such a quasi-one-dimensional scenario is typical for atoms and molecules [11] in strong magnetic fields. It has also been reported for electron-hole pairs in a semiconductor at high magnetic fields [12] and for long-range molecules formed by a ground state and a Rydberg atom [13]. The effective Hamiltonian for the longitudinal dynamics is obtained by $H_{\parallel} = \int d\phi \int d\rho \rho \Theta_{0,0}^*(\rho, \phi) H_{\text{el}} \Theta_{0,0}(\rho, \phi)$. Neglecting a constant energy offset, one obtains

$$H_{\parallel} = \frac{p_z^2}{2m} - \frac{e^2}{2\pi\epsilon_0} \frac{\sqrt{\pi}}{\rho_0} \sum_{k=1}^2 \exp[(z - Z_{0,k})^2/\rho_0^2] \\ \times \text{erfc}\left(\frac{|z - Z_{0,k}|}{\rho_0}\right) - \frac{1}{2} m \Omega_z^2 z^2, \quad (4)$$

where $\Omega_z = 2\sqrt{(e\beta)/m} = 2\pi \times 189$ MHz is the ‘‘frequency’’ of the inverted parabolic potential and $\text{erfc}(x)$ is the complementary error function. The corresponding longitudinal potential is presented in Fig. 1. If the electron is far away from

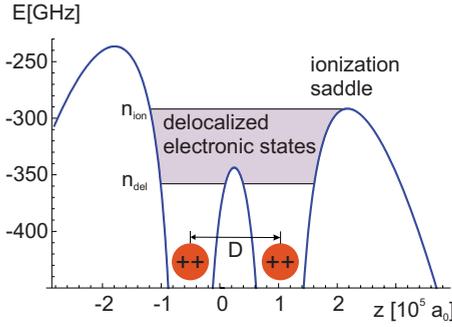


FIG. 1. (Color online) Electronic potential if the ions are frozen at their equilibrium positions of the configuration $A^{++}+A^+$. The electronic potential supports bound states which are delocalized between the two nuclei. For too large excitation energies the saddle point due to the inverted harmonic potential leads to field ionization.

either ionic core, the potential is approximately a sum of two one-dimensional Coulomb potentials $V_{1D} = -e^2/(2\pi\epsilon_0|z|)$ centered at the respective ionic equilibrium positions. For small excitation energies the potential wells are well separated. If the excitation energy surpasses $E_{del} \approx -(2e^2)/(\pi\epsilon_0 D)$, the wells merge and hence electronic states which extend over both ionic cores are possible. Expressing E_{del} in terms of the principal quantum number n , one finds this merging to occur at $n_{del} \approx (e/\hbar)\sqrt{(mD)/(16\pi\epsilon_0)}$. For the employed parameter set one finds the numerical value $n_{del} = 195.654$ [14], which is significantly smaller than the principal quantum number we obtained earlier by invoking the argument of overlapping wave functions. Further inspection of the potential reveals that the inverted parabolic potential due to the Penning trap eventually leads to field ionization, which is shown in Fig. 1. The position of the saddle ($z_{sd} > Z_{0,2}$) is given by $z_{sd} = \gamma Z_{0,2}$, where $\gamma > 1$ is the solution of the equation $(\gamma - 1)^{-2} + (\gamma + 1/2)^{-2} - \sigma\gamma = 0$ and $\sigma = [(1/2)m\Omega_z^2 Z_{0,2}^2][e^2/(4\pi\epsilon_0|Z_{0,2}|)]^{-1} = (1/2)Q_1^3/(Q_1 + Q_2)^2 = 4/9$. This equation is solved by $\gamma = 2.12$, and thus the saddle point is for our parameters located at $z_{sd} = 217\,523a_0$. From this we find that classically ionization is expected to occur beyond energies corresponding to the principal quantum number $n_{ion} = 1.456\sqrt{Z_{0,2}/a_0} = (0.21e^{2/3}\sqrt{m})/(\hbar\epsilon_0^{2/3}\beta^{1/6}) \approx 466$. Hence there is an energy window $n_{del} < n < n_{ion}$ in which delocalized electronic states exist. Here the escape of the electron from the trap is prevented by its attraction to the doubly charged ion. For the given parameters the width of this window is about $\hbar 2\pi \times 60$ GHz.

We now focus on the electronic states which lie close to the top of the Coulomb barrier. Since for these states the asymmetry of the electronic potential due to the anticonfining is small, it makes sense to define gerade and ungerade states with respect to the approximate symmetry point $z_{sym} = (Z_{0,1} + Z_{0,2})/2$. In Fig. 2 we show a sketch of the energy-level structure of Hamiltonian (4) in the vicinity of n_{del} . Gerade ($|E_g\rangle$) and ungerade ($|E_u\rangle$) states are energetically split by the energy $2\hbar\kappa = E_u - E_g$, with κ being the tunnel coupling. The splitting increases with increasing degree of excitation. States which are localized in the left ($|E_l\rangle$) or right

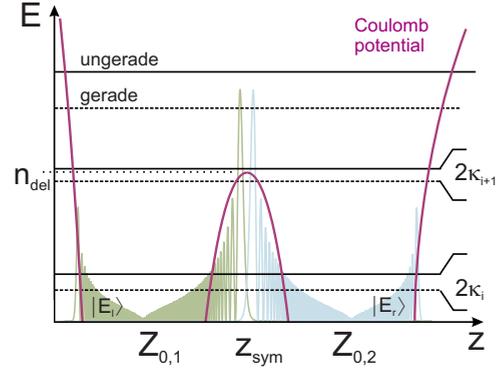


FIG. 2. (Color online) Sketch of the energy-level structure close to n_{del} . Here the influence of the inverted parabolic potential can be approximately neglected and the states can be characterized by their symmetry property under reflection at z_{sym} . The energies of these pairs of gerade (ungerade) states are indicated by dashed (solid) lines. The pairs are almost degenerate with a small energy splitting κ_i . Wave functions which are localized in one of the two wells ($|E_{l/r}\rangle$) can be created by linear superpositions of the gerade and ungerade states. Examples of two such wave functions are shown.

well ($|E_r\rangle$) can be created by the linear combinations $|E_l\rangle = (1/\sqrt{2})[|E_g\rangle + |E_u\rangle]$ and $|E_r\rangle = (1/\sqrt{2})[|E_g\rangle - |E_u\rangle]$, respectively. They are not stationary, but evolve under the Hamiltonian $H_{tunnel} = \hbar\kappa(|E_l\rangle\langle E_r| + \text{H.c.})$, which describes Rabi oscillations of the electronic density between the left and right wells at a rate κ . As an example we provide two sets of gerade and ungerade eigenstates, which were obtained for the above parameters: their energies correspond to the principal quantum numbers $n_g^{(1)} = 195.318$, $n_u^{(1)} = 195.335$ and $n_g^{(2)} = 195.599$, $n_u^{(2)} = 195.668$. The tunnel coupling in the two cases evaluates to $\kappa_1 = 2\pi \times 29.5$ MHz and $\kappa_2 = 2\pi \times 121.2$ MHz. Since these rates are significantly larger than the oscillation frequencies of the ionic cores, it is indeed justified to use the picture of a frozen ionic motion. Moreover, the rates are much larger than the radiative decay rate of Rydberg states, which is usually smaller than 1 MHz [10]. Therefore the described process can be considered coherent.

We are now in position to study the charge-transfer process $A^{++}+A^+ \rightarrow A^++A^{++}$. To this end we employ two laser fields coupling the ground state of the right ion $|G_r\rangle$ resonantly to the state $|E_r\rangle$ with a Rabi frequency Ω_2 . Due to the tunnel coupling, the state $|E_r\rangle$ evolves into the state $|E_l\rangle$, which is then resonantly coupled to the ground state $|G_l\rangle$ of the left ion with Rabi frequency Ω_1 . During the charge transfer, the external positions of the ions are frozen. Hence, the external state of the final configuration A^++A^{++} will be displaced from its equilibrium. The corresponding energy offset—i.e., the change in potential energy $\hbar\Delta$ —has to be accounted for in order to make the transition $|E_l\rangle \rightarrow |G_l\rangle$ resonant. This is shown in Fig. 3 where the potentials of the ground-state configurations $A^{++}+A^+$ and A^++A^{++} are depicted. The intersections shown are made along the normal coordinate $Z_a = \alpha_- Z_1 + \alpha_+ Z_2$ at $Z_b = -\alpha_+ Z_1 + \alpha_- Z_2$ set to zero. The coefficients are given by $\alpha_{\pm} = \sqrt{(1/2) \pm 3/(2\sqrt{73})}$. The energy gap between the two configurations evaluates to $\hbar\Delta = (e\beta\zeta^2)/(2 \times 3^{1/3})$, which yields for our parameters $\Delta = 2\pi \times 21.4$ GHz.

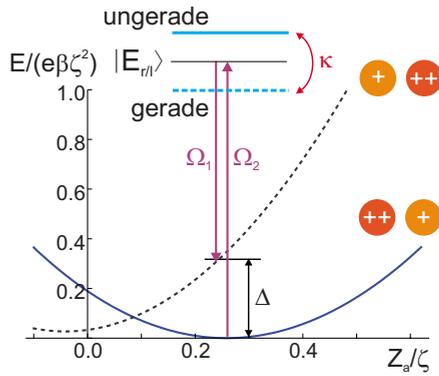


FIG. 3. (Color online) Cut through the external potential along the normal coordinate Z_a with $Z_b=0$. The equilibrium positions of the initial configuration ($A^{++}+A^+$) do not coincide with those of the final configuration (A^++A^{++}). As a consequence, there is a relative detuning Δ between the initial and final states which has to be accounted for during the laser excitation.

With the two lasers turned on and choosing $\Omega_1=\Omega_2=\Omega$, the electronic dynamics is governed by the Hamiltonian

$$H_{\text{unn}}/\hbar = \Omega|G_l\rangle\langle E_l| + \Omega|G_r\rangle\langle E_r| + \kappa|E_l\rangle\langle E_r| + \text{H.c.}, \quad (5)$$

where $|G_{r/l}\rangle$ is the ground state of a *singly charged* ion at the left or right position in the trap. The probability of finding the electron in the left potential well is given by

$$p_{\text{left}}(t) = \frac{1}{1+4\delta^2} \{ \delta^2 [\cos(\epsilon_- \kappa t) - \cos(\epsilon_+ \kappa t)]^2 + [\epsilon_+ \sin(\epsilon_- \kappa t) - \epsilon_- \sin(\epsilon_+ \kappa t)]^2 \},$$

with $\epsilon_{\pm} = \sqrt{(1+2\delta \pm \sqrt{1+4\delta^2})/2}$ and $\delta = \Omega/\kappa$. In Fig. 4 this probability is shown for three different values of δ . For $\delta = 0.2$ the electron mainly stays with the right ion over the time interval shown. As δ increases, the likelihood to find the electron in the left well increases significantly for small times. In the limit $\delta \gg 1$ one finds $p_{\text{left}}(t) = (1/2)[1 - \cos(\kappa t)]$

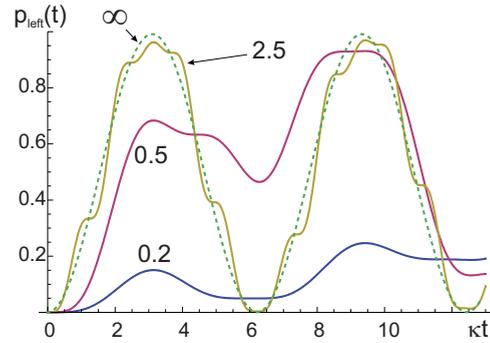


FIG. 4. (Color online) Time dependence of the probability to find the electron with the left ion for $\delta=0.2, 0.5, 2.5$ and the asymptotic curve for $\delta \gg 1$. Initially the electron is with the right ion. The time evolution is governed by the Hamiltonian (5).

and the electron is found with certainty to be with the left ion at the times $t_m = (2m+1)\pi/\kappa$. Once the transfer is performed and the lasers are switched off, the system is in a vibrationally highly excited state as can be seen from the potential surfaces presented in Fig. 3. A successful charge transfer, which can be monitored by fluorescence imaging on a frequency which is only resonant on a transition of the singly charged ion, will be accompanied by strong oscillations of the ions. Apart from the complete transfer it is also possible to create coherent superpositions of the states $A^{++}+A^+$ and A^++A^{++} . Thereby a large motional Schrödinger cat state can be realized. Since the dipole moments of the corresponding configurations differ by approximately $e\zeta = 5 \times 10^5$ D, coherent superpositions of two macroscopically different dipoles are achieved.

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