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Hetero charged ion clusters in a Paul trap

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We prove that stable Coulomb clusters consisting of ions of both signs of charge exist in a Paul trap.

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In 1959, Wuerker, Shelton and Langmuir [1] observed repeated crystallization and melting of charged aluminum particles in a Paul trap [2–4]. In the "crystalline phase" the particles are arranged in regular geometric patterns. Melting of the structures resulted in the formation of a chaotic cloud of aluminum particles. Only very recently and based on advances in laser cooling and photon imaging techniques, stable ion crystals as well as transitions between the crystalline and the cloud phase were observed experimentally [5]. Several other groups have confirmed the existence of stable clusters of ions [6–8]. Ions of only one sign of charge are used in these experiments. The question arises whether stable ion clusters consisting of ions of both charge signs can exist in a Paul trap. It is proved here that a light positively (negatively) charged ion and two heavy negatively (positively) charged ions indeed form a dynamically stable "crystalline" configuration in a Paul trap.

A Paul trap is an electro dynamical device for the stable confinement of charged particles. It consists of a ring electrode and two polar end caps and has proven to be an indispensible device for the investigation of single isolated ions [9–13]. It also exhibits interesting dynamical effects if more than one ion is stored in the trap, including phenomena like dynamical phase transitions [5, 14] and chaos [7, 14, 15]. The electric potential experienced by an ion stored in a Paul trap is of the quadrupole type and given explicitly by [2]

$$\Phi(\mathbf{r})=\frac{U_0+V_0\cos(\Omega t)}{r_0^2+2z_0^2}(x^2+y^2-2z^2). \tag{1}$$

Here, $\mathbf{r}=(x, y, z)$ is the position vector of the ion with respect to the geometrical center of the trap, U_0 is the dc voltage applied to the trap, V_0 is the amplitude of the ac voltage, Ω is the angular frequency of the applied ac voltage, r_0 is the radius of the ring electrode of the Paul trap and z_0 is half the distance between the trap's end caps.

Assume that there are $i=1, 2, \ldots, N$ ions in the trap interacting via their Coulomb forces. The masses of the ions are denoted by $m_i \cdot u$ and the charges by $Z_i \cdot e$. Here, u is the atomic mass unit ($u=1.66\cdot 10^{-27}$ kg) and e is the elementary charge ($e=1.60\cdot 10^{-19}$ C). We use SI units throughout. The classical equations of motion of the N particles are given by the following set of $3N$ coupled nonlinear equations

$$u\cdot m_i\frac{d^2}{dt^2}\begin{pmatrix}x_i\\ y_i\\ z_i\end{pmatrix}=-2eZ_i\frac{U_0+V_0\cos(\Omega t)}{r_0^2+2z_0^2}\begin{pmatrix}x_i\\ y_i\\ -2z_i\end{pmatrix}+\frac{e^2}{4\pi\varepsilon_0}Z_i\sum_{j\neq i}Z_j\frac{\mathbf{r}_i-\mathbf{r}_j}{|\mathbf{r}_i-\mathbf{r}_j|^3} \tag{2}$$

where $\varepsilon_0=8.85\cdot 10^{-12}\,[\mathrm{N}\cdot\mathrm{m}^2/\mathrm{C}^2]^{-1}$ is the dielectric constant. With the help of the dimensionless quantities

$$a_0=\frac{8eU_0}{u\Omega^2(r_0^2+2z_0^2)};\qquad q_0=\frac{4eV_0}{u\Omega^2(r_0^2+2z_0^2)} \tag{3}$$

$$a^{(i)}=\frac{Z_i}{m_i}a_0;\qquad q^{(i)}=\frac{Z_i}{m_i}q_0;\qquad \tau=\Omega t/2 \tag{4}$$

$$s^{(i)}=\frac{e^2Z_i}{m_i\Omega^2\pi u\varepsilon_0}\left(\frac{1}{1\,\mu\mathrm{m}}\right)^3 \tag{5}$$

the equations of motion (2) can be written as

$$\frac{\mathrm{d}^2}{\mathrm{d}\tau^2}\begin{pmatrix}x_i\\ y_i\\ z_i\end{pmatrix}=-[a^{(i)}+2q^{(i)}\cos(2\tau)]\begin{pmatrix}x_i\\ y_i\\ -2z_i\end{pmatrix}+s^{(i)}\sum_{j\neq i}Z_j\frac{\mathbf{r}_i-\mathbf{r}_j}{|\mathbf{r}_i-\mathbf{r}_j|^3}. \tag{6}$$

The position coordinates in (6) are in units of μm. For noninteracting ions, i.e., $s^{(i)}=0$ in (6), the motion of the ions is described by a set of $3N$ decoupled Mathieu equations. Using Floquet analysis [16–18] it can be shown that the motion of a trapped ion is composed of a superposition of a slow "secular" oscillation with frequencies

$$\omega_x^{(i)}=\omega_y^{(i)}=\mu_x^{(i)}\,\Omega/2; \quad \omega_z^{(i)}=\mu_z^{(i)}\,\Omega/2 \tag{7}$$

in x, y and z direction, respectively, and a fast "micro motion" at the trap frequency Ω. For small $a^{(i)}$ and $q^{(i)}$, the Floquet exponents $\mu_x^{(i)}$ and $\mu_z^{(i)}$ in (7) are given by [2, 15]

$$\mu_x^{(i)}=[a^{(i)}+\tfrac{1}{2}q^{(i)2}]^{1/2}; \quad \mu_z^{(i)}=[2(q^{(i)2}-a^{(i)})]^{1/2}. \tag{8}$$

Thus, the i'th ion moves effectively in the (anisotropic) harmonic oscillator potential (secular oscillator)

$$V_S(\mathbf{r})=\tfrac{1}{2}m_i u(\omega_x^2 x^2+\omega_y^2 y^2+\omega_z^2 z^2) \tag{9}$$

whose principal axes coincide with the x, y and z axes of the trap. All Paul traps described in the literature are axially symmetric with respect to the z axis. This is the reason for $\omega_x=\omega_y$ in (7). With the picture of the secular oscillator in mind, equilibrium shapes of ionic structures in a Paul trap can easily be understood as the minimal energy configurations of the ions in the potential (9) [3, 19]. So far, only ions with the same charge polarity were shown to form stable crystals of typical dimensions in the μm regime. It is much harder to imagine stable μm size crystals consisting of ions with both signs of charge. In this case, both, the attractive Coulomb force between ions of different charge signs and the focusing trap potential will try to collapse the system. There is, however, a way to play the trap's focusing force and the ions' attractive and repulsive Coulomb forces one against the other and to achieve a classically stable crystalline configuration. The resulting ion structure consists of two heavy negatively (positively) charged ions symmetrically positioned with respect to the trap center and one light, positively (negatively) charged ion located at the center of the trap. The situation is depicted in Fig. 1a, which shows the three ions (A: light, positively charged; B, C: heavy, negatively charged) aligned on the x axis. The idea is that for the ion arrangement in Fig. 1a, the sum of the ions' Coulomb forces and the trap's focusing force is a double hump potential with a local minimum at the origin. Thus, the central ion close to the origin is trapped in the potential pocket. We are now investigating this situation in detail. Assume that there are two ion species in the trap. An ion A with mass $m\cdot u$ and charge $+Qe$ and two other identical ions, B and C, with mass $M\cdot u$ and charge $-Z\cdot e$. In order to keep our arguments simple, we will, for the time being, assume $a^{(i)}=0$. The motivation for investigating the configuration shown in Fig. 1a is derived from the following three arguments: *(i)* For $a^{(i)}=0$ it follows from (7) and (8) that $\omega_z^{(i)}\approx 2\omega_x^{(i)}$, i.e., the secular oscillator is steeper in z direction. For a small number of stored ions, the minimal energy configurations are therefore expected to be planar structures in the $x-y$ plane. This is confirmed experimentally [3, 5, 14, 15]. We assume, therefore, that A, B and C have to lie in the $x-y$ plane in order to achieve stability. *(ii)* Because of the Coulomb repulsion of the ions B and C, the three ions will most likely prefer a stretched configuration with ion A in the middle for symmetry reasons. *(iii)* Because of the above-mentioned axial symmetry of the Paul trap, there is no loss of generality if we assume that the stretched ion configuration is aligned with the x axis.

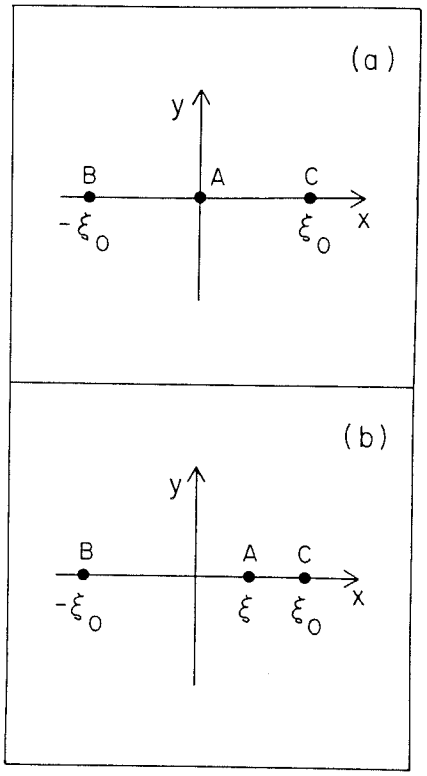

Fig. 1. a Stable equilibrium configuration of three ions A, B, C in the $x-y$ plane of a Paul trap. Ion A is located at the origin and characterized by a small mass m and charge $-Q$. Ions B and C, located at $x=-\xi_0$ and $x=\xi_0$, respectively, have a large mass M and charge Z. **b** Ion A displaced a distance ξ from the origin for stability investigations

Neglecting the micro motion of the ions, we will now derive the various conditions under which the configuration shown in Fig. 1a is stable. In equilibrium, ions B and C are located at $x=-\xi_0$ and $x=\xi_0$, respectively. The forces acting on ion C are in equilibrium, if the Coulomb forces acting on C and the trap's focusing force balance out:

$$-Mu(\omega_x^{(C)})^2\,\xi_0-\frac{ZQe^2}{4\pi\varepsilon_0}\frac{1}{\xi_0^2}+\frac{Z^2e^2}{4\pi\varepsilon_0}\frac{1}{4\xi_0^2}=0. \tag{10}$$

Equation (10) has a solution $\xi_0>0$ only if

$$Z>4Q. \tag{11}$$

This is a necessary condition for the stability of a hetero-3-cluster. If it is fulfilled, the equilibrium position ξ_0 of ion C ($-\xi_0$ for ion B) is given by

$$\xi_0 = \left[\frac{2Me^2}{u\pi\varepsilon_0 \Omega^2 q_0^2}\left(\frac{1}{4}-\frac{Q}{Z}\right)\right]^{1/3}. \tag{12}$$

A second condition is derived by requiring that the structure in Fig. 1a is stable under small perturbations of the equilibrium position of ion A. Assume that the charges B and C are frozen at $x=-\xi_0$ and $x=\xi_0$, respectively, and the position of ion A is given by $x=\xi$ (see Fig. 1b). Just like in the case of ion C, there are two types of forces acting on ion A: the Coulomb force due to ions B and C and the trap's focusing force. For small displacements ξ the Coulomb force is given by

$$F_C(\xi) = \frac{QZe^2}{4\pi\varepsilon_0}\frac{4}{\xi_0^3}\xi. \tag{13}$$

Whereas the focusing force is given by:

$$F_S(\xi) = -m\cdot u\cdot(\omega_x^{(A)})^2\,\xi. \tag{14}$$

In order for the focusing force to win out over the Coulomb force, we must have

$$mu(\omega_x^{(A)})^2 > \frac{QZe^2}{4\pi\varepsilon_0}\frac{4}{\xi_0^3} \tag{15}$$

or

$$16\frac{m}{M}\frac{\eta^2}{\eta-4} < 1. \tag{16}$$

We introduced the charge ratio $\eta = Z/Q$. For given mass ratio m/M, the left hand side of (16) is a minimum for $\eta = 8$. Therefore, the maximal range of allowed mass ratios is given by

$$\frac{m}{M} < 1/256. \tag{17}$$

Not even the largest allowed mass ratio, i.e. $m/M \approx 1/256$, can be accomplished with the known stable atomic ions. On the other hand, (17) is easily fulfilled with (organic) molecular ions or charged clusters.

Experimentally it would probably be most convenient to have a negatively charged ion at the center of the trap and two heavy positively charged molecules or clusters at the positions B and C. But in order to be specific, let us choose a proton for ion A and some molecule of atomic mass 500 for the ions B and C which are assumed to carry five negative charges – keeping in mind that for experimental convenience the signs of the charges can always be reversed if necessary. Also we fix $q_0 = 0.2$ and $f = \Omega/2\pi = 10$ MHz. For this special choice of parameters, the equilibrium distance of the ions is given by $\xi_0 = 56\,\mu$m. If positions are measured in μm and energies in meV, then the secular potential acting on the proton is given by

$$V_S(x) = 1.02\cdot 10^{-4}\,x^2 \tag{18}$$

and the total Coulomb potential acting on the proton is given by

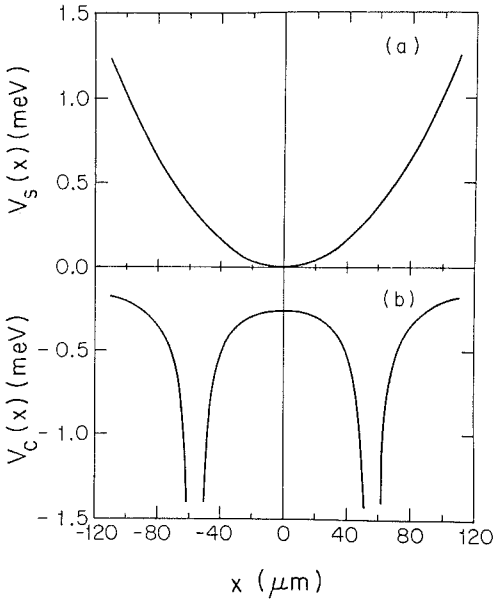

Fig. 2a, b. The two types of potentials acting on the central ion A. **a** The secular oscillator potential and **b** the Coulomb potential originating from the interaction with ions B and C which are assumed to be frozen at $-\xi_0$ and ξ_0, respectively, with $\xi_0 = 56\,\mu$m

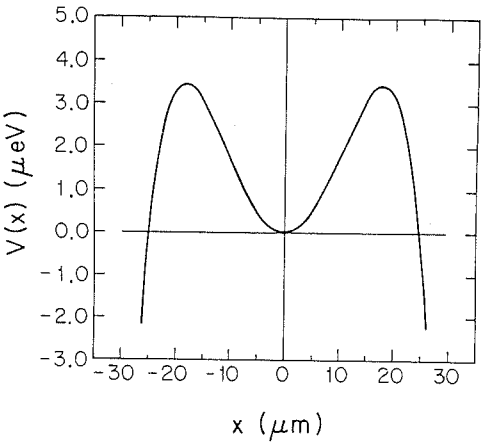

Fig. 3. The total time averaged potential $V(x) = V_S(x) + V_C(x)$ acting on the central ion A

$$V_C(x) = -7.19\left[\frac{1}{|\xi_0+x|}+\frac{1}{|\xi_0-x|}\right]. \tag{19}$$

The two potentials are shown in Fig. 2a and in Fig. 2b, respectively. The total potential

$$V(x) = V_C(x) + V_S(x) \tag{20}$$

acting on the proton is the result of a delicate cancellation of potentials at the origin and shown in Fig. 3. As a result of the cancellations the energy scale in Fig. 3 is μeV. As suggested in the introduction, $V(x)$ indeed shows a double hump structure. The height of the barrier which confines the proton to the vicinity of the origin is of the order of 3.5 μeV. The maximum of the barrier is located at $\xi_b \approx 18\,\mu$m. Due to the cancellations, the barrier height is a very sensitive function of the numerical

factors appearing in (18) and (19). A 1% change in one of the numerical factors in (18) or (19) results in an approximately 10% change in the barrier height!

It is interesting to note that the potential pocket in $V(x)$, although appearing rather shallow, nevertheless binds several thousand quantum states. Assuming that the pocket is a harmonic oscillator with a potential height of E_b at ξ_b, the pocket binds

$$N_b = \frac{\xi_b}{\hbar}\sqrt{E_b\, mu/2} \tag{21}$$

states of a particle with atomic mass m. In our case this corresponds to 3700 bound proton states. Moreover this argument shows that due to the large quantum numbers involved, a classical treatment of the three ion system is justified. The temperature of the system has to be lower than $T=40$ mK so that the proton is not instantaneously heated over the barrier.

So far we discussed only stability in x direction. For fixed ions B and C stability in y and z direction is guaranteed since both the Coulomb force and the focusing trap force try to pull the ion A toward the origin. Therefore, the maxima in Fig. 3 correspond to saddle points of the three dimensional potential acting on ion A.

In an attempt to include the effects of the micro motion we integrated numerically the coupled system of equations (6) for the specific example discussed above. In these calculations all three ions were free to move in all three spatial directions and were subjected to the time varying trap potential as well as to their mutual Coulomb forces. We added an additional damping term $-\gamma \cdot \mathrm{d}\mathbf{r}_i/\mathrm{d}\tau$ to the equations of motion to simulate (laser) cooling. The damping constant γ was $\gamma=0.01$. For various initial conditions, the system (6) was integrated over 200 cycles of the trap field. The initial conditions consisted of random displacements of ions, A, B and C about their equilibrium positions at time $\tau=0$. The magnitude of the displacements ranged from 0.1 to 2 μm. All initial velocities were set to zero. In all the cases studied, the solutions of (6) were stable over 200 cycles. Moreover, the solutions, under the influence of the damping term, showed a tendency to approach the above calculated equilibrium values $-\xi_0, 0$ and ξ_0, respectively. Even without damping and small initial displacements ($\Delta x, \Delta y, \Delta z \leqq 0.5$ μm) the solutions were stable over at least 200 cycles of the trap field showing quasi periodic oscillations. Thus, we demonstrated that stable ion configurations consisting of three ions of both charge types do indeed exist in a Paul trap.

Several directions are now open for further investigations:

a) Switching on the dc voltage does not change the collapse condition (11), but leads to a significantly modified stability condition (17). The equilibrium distance with dc voltage becomes

$$\xi_0 = \left[\frac{Ze^2}{u\pi\varepsilon_0\,\Omega^2\left(-a_0+\frac{Z}{2M}\,q_0^2\right)}\left(\frac{1}{4}-\frac{Q}{Z}\right)\right]^{1/3} \tag{12'}$$

and the stability condition (16) reads:

$$\frac{16}{1-4Q/Z}\,\frac{-a_0+\frac{Z}{2M}\,q_0^2}{a_0+\frac{Q}{2m}\,q_0^2}<1. \tag{16'}$$

At a first glance at (16') it appears that (16') can always be fulfilled with the choice

$$a_0=\frac{1}{2}\,\frac{Z}{M}\,q_0^2. \tag{22}$$

This is equivalent to operating the ion trap at the dynamical stability limit with respect to the ions B and C. On the other hand the trap has to be stable for the ion A as well which requires

$$a^{(A)}+\tfrac{1}{2}\,q^{(A)^2}>0 \tag{23a}$$

$$q^{(A)^2}-a^{(A)}>0. \tag{23b}$$

The conditions (23a) and (23b) express the fact that the trap becomes unstable if the Floquet exponents μ_x or μ_z, or both, become complex. The conditions (23) are then a direct consequence of (9). Since $a^{(A)}$ is positive, (23a) is trivially fulfilled. The condition (23b), however, demands

$$\left(\frac{Q}{m}\,q_0\right)^2-\frac{QZ}{2mM}\,q_0^2>0 \tag{24}$$

or

$$\frac{mZ}{2MQ}<1. \tag{17'}$$

This condition is much less stringent than (17). For $Q=1$ and $Z=5$ it can be met easily even with atomic ions.

b) Ion clusters consisting of an ion with charge Qe at the center of the trap and three ions of charge $-Ze$ grouped around it in the form of an equilateral triangle should also be stable under appropriate conditions. Analogous configurations consisting of four or five ions of charge $-Ze$ grouped around the central ion with charge Qe can be imagined. Depending on the choice of the applied voltages even 3D configurations are possible for more than three outer ions.

c) Hetero charged clusters might also be stabilized by applying an additional homogeneous electric field, or by spinning up the outer ions (e.g. by radiation pressure originating from a slightly displaced cooling laser [3]. The idea that angular momentum is helpful for stabilizing hetero clusters stems from considering equation (15). If a net angular momentum is present, the centrifugal force will tend to increase the equilibrium distance ξ_0. Thus, (15) can be fulfilled with larger m resulting in a larger (and more favorable) mass ratio m/M.

d) The central ion is confined in a non-linear double hump potential and – if displaced from the origin – is driven by the ac field of the trap (micro motion). Driven non-linear oscillators are prone to exhibit deterministic

chaos [20] and the possible onset of chaotic motion in this driven system could be studied. If the central ion performs a transition to chaos, the resulting chaotic heating (rf heating) has to be counterbalanced by appropriate (laser) cooling. We did not yet investigate the phase space trajectories of the ions A, B and C in detail. Qualitatively, however, the conjecture of a possible chaos transition in the three ion hetero cluster is supported by the results of the above-mentioned microscopic simulations. For large initial displacements (but still well inside the potential pocket), Poincaré sections of ion A phase space do not show any discernable regularity.

e) Instead of a light positively charged ion at the origin, and two heavy negatively charged ions outside, one could choose an electron as the central charge and two positively charged ions at positions $-\xi_0$ and ξ_0, respectively. Since the electron is very light, even the condition (17) (no dc voltage present) can be fulfilled easily with atomic ions as the outer charges. The question of quantum motion in the pocket of the double hump potential becomes even more interesting in this case, since for given barrier height and due to the small mass of the electron, the potential pocket binds far fewer electron states. A difficulty in this case arises from the small mass of the electron. A rather high frequency has to be applied to the trap in order to assure stable confinement.

f) If different ion species are used for ion A and ions B, C respectively, optical cooling transitions will most likely have vastly different frequencies. Two different lasers are then necessary to cool the system. In some cases, like the special example treated above, or the use of an electron as the central charge (see e)), the central ion (electron) cannot be cooled optically at all. One could then try to cool strongly the ions B and C and rely on sympathetic cooling [21] for the central ion A.

In conclusion it is suggested that hetero charged (ion/electron) clusters of the types described above be used in quantum tunneling experiments to shed more light on the nowadays much discussed question of (chaotic) tunneling in non-integrable potentials. The difficult part in this investigation is to set up the hetero cluster experimentally. Here the following suggestion might help: The trap has to be loaded sequentially. First the light central ion is loaded into the trap and placed at the origin by reducing its kinetic energy with the various atomic cooling procedures nowadays available. Only then, the heavy ions are loaded into the trap. The reverse procedure does not work since even if the heavy ions are firmly placed at their equilibrium positions B and C respectively, the strong Coulomb forces will make it virtually impossible for the light ion to find its path to the origin of the trap.

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