Quantum control of quantum triple collisions in a maximally symmetric three-body Coulomb problem

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Abstract

In Coulomb 3-body problems, configurations of close proximity of the particles are classically unstable. In confined systems they might however exist as excited quantum states. By studying a maximally symmetric subspace of the 3-body problem one obtains strong evidence for the existence of excited states for which the wave function is non-zero for triple collision configurations. Quantum control of such states by time changing electromagnetic fields is discussed, with particular emphasis on the nature of the required controls.

Availability of appropriately shaped laser pulses at very short time scales provides a tool to control molecular dynamics. Quantum control applications range from multi-photon excitations to direct control of chemical reactions and to many diverse designs in quantum information [1] [2] [3] [4] [5]. By quantum control one might also be able to excite exotic quantum states, in particular in confined systems [6]. One type of such states are the *scar* states [7] [8] [9] which correspond to classically unstable configurations, but may appear as well defined states in the quantum spectrum.

This paper is concerned with a 3-body Coulomb problem of two positively charged particles of mass M and charge Ze and a negatively charged one of mass m and charge qe. Let $\widetilde{R}$ be the separation of the positive particles, $\widetilde{\rho}$ the distance of the negative particle to one of the positive ones and $\psi\left(\widetilde{R},\widetilde{\rho}\right)$ the system wave function. The central question to be addressed is whether there are excited states for which $\psi\left(0,0\right)\neq 0$. Such states will be called *quantum triple collisions* (QTC). Practical applications of this study concern the question of how to counter, by quantum control, potential barriers in molecular [6] or nuclear reactions in confined systems [10].

In the case of two heavy (M) and one light (m) particle, it is more or less obvious, from kinetic barrier considerations, that such states, if they exist,

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should be relatively high in the spectrum. Of course, in Coulomb systems in free space such energies would be expected to correspond to scattering states. Therefore the search for quantum triple collisions in Coulomb systems only makes sense for systems that are confined, for example, in a metalic lattice.

The full system has 9 spatial degrees of freedom. For the full system one may at most reduce this number to three by fixing the two positive charges in one direction ($\widetilde{R}$) and describing the negative charge in cylindrical coordinates $(\widetilde{\rho},\theta)$. However, the purpose here is not to describe the full spectrum of the problem, but to discuss the existence or non-existence of quantum triple collisions. Therefore one may look for them in a reduced subspace of *maximally symmetric states*, which would correspond to states symmetric in the θ coordinate. Existence of QTC states in this subspace is not a necessary condition for their existence in the full system, but it is a sufficient one. For the exploration of this maximally symmetric subspace of states the number of degrees of freedom may be reduced to two.

Take one of the positively charged particles as the origin and use spherical coordinates for the other two particles. The full Hilbert space measure is

$$d\nu = \widetilde{R}^2 d\widetilde{R} d\Omega_+ \widetilde{\rho}^2 d\widetilde{\rho} d\left(\cos\theta\right) d\varphi \tag{1}$$

$\left(\widetilde{R},\Omega_+\right)$ being the coordinates of the second positively charged particle and $(\widetilde{\rho},\theta,\varphi)$ those of the negatively charged one. The Hamiltonian is

$$\widetilde{H} = -\frac{\hbar^2}{2M}\frac{1}{\widetilde{R}^2}\frac{\partial}{\partial\widetilde{R}}\left(\widetilde{R}^2\frac{\partial}{\partial\widetilde{R}}\right) - \frac{\hbar^2}{2m}\frac{1}{\widetilde{\rho}^2}\frac{\partial}{\partial\widetilde{\rho}}\left(\widetilde{\rho}^2\frac{\partial}{\partial\widetilde{\rho}}\right) + V\left(\widetilde{R},\widetilde{\rho},\theta\right) \tag{2}$$

$$V\left(\widetilde{R},\widetilde{\rho},\theta\right) = \frac{Z^2e^2}{4\pi\varepsilon_0}\frac{1}{\widetilde{R}} - \frac{Zqe^2}{4\pi\varepsilon_0}\left\{\frac{1}{\widetilde{\rho}} + \frac{1}{\sqrt{\widetilde{R}^2+\widetilde{\rho}^2-2\widetilde{R}\widetilde{\rho}\cos\theta}}\right\} \tag{3}$$

Let

$$\begin{aligned} \mu &= \frac{m}{M} \\ G^2 &= \frac{Zme^2}{2\pi\varepsilon_0\hbar^2} \end{aligned} \tag{4}$$

and redefine

$$R = G^2\widetilde{R};\ \rho = G^2\widetilde{\rho};\ H = \frac{2m}{\hbar^2G^4}\widetilde{H} \tag{5}$$

μ, R, ρ and H being dimensionless quantities, the results may easily be used both for molecular and nuclear environments. Maximally symmetric states, as defined above, being independent of the θ coordinate, an equivalent Hamiltonian H acting in their subspace, is obtained by integration over the $\theta-$angle variables obtaining

$$H = \frac{2m}{\hbar^2G^4}\widetilde{H} = -\mu\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) - \frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial}{\partial\rho}\right) + \frac{Z}{R} - \frac{q}{\rho} - q\left\{\frac{\chi\left(R-\rho\right)}{R} + \frac{\chi\left(\rho-R\right)}{\rho}\right\}, \tag{6}$$

χ being the Heaviside function[1]. Then, the maximally symmetric subsystem has two degrees of freedom with integration measure

$$d\sigma = R^2 dR^2 \rho^2 d\rho \tag{7}$$

From (6) one sees that, in spite of the Coulomb barrier between the positive charges ($\frac{Z}{R}$), the effective potential in the subspace of maximally symmetric states, becomes attractive in the region $\rho < R$ if $\rho < \frac{q}{Z-q} R$. Given an eigenstate $\psi(R, \rho)$ of H, the quantum probability for a two-body collision of the positively charged particles is proportional to

$$I_2 = \int d\rho \rho^2 \left|\psi(0, \rho)\right|^2 \tag{8}$$

and, as defined above, there is a quantum triple-collision if $\psi(0,0) \neq 0$.

A difficulty on the way to a rigorous solution to this problem is the fact that the potential is singular at the $R = \rho = 0$ point. In an actual physical system this point could never be reached because of the finite dimensions of the particles. Therefore a reasonable approximation that avoids the singularity problem is to compute the numerical solution of the spectrum in a grid that does not contain the $R = \rho = 0$ point, with the average of ψ on the smallest square around the origin standing for $\psi(0,0)$. Because of the Coulomb barrier and the kinematical cost of localization, it is to be expected that the quantum triple collision states, if they exist, will be relatively high in the spectrum. Therefore to compute them one needs a method that involves very many basis states. A simple way to fulfill this requirement is to represent the operator H in a fine grid of points in a box[2] of size $[0, L]^2$ and to diagonalize the resulting matrix. As far as I know, this is the best way to obtain both the ground and high excited states with similar degrees of accuracy. The number of eigenstates that is obtained equals the number of points in the grid. However the number of different, discrete spectrum, energy levels of the confined system is much smaller, wave functions at each level being related by symmetry transformations. As a result, when fine grids are used, the energy spectrum has a piecewise constant nature.

The Fig.1 shows the results of such calculation for[3] $\mu = 2.7 \times 10^{-4}$. The upper left panel is the value of $\psi(0,0)$ along the spectrum. One sees that for all the lower part of the spectrum this is a vanishing value, although for high excitation values there are many quantum triple collision states (QTC). These states are many, but still somewhat exceptional in the whole set.

The right upper panel shows the *energy difference* Δ between the ground state ψ_0 and the excited states (in H units) and the two lower panels show,

[1] $\chi(x) = 1$ for $x \geq 0$, $\chi(x) = 0$ for $x < 0$

[2] Because one is using spherical coordinates this box size corresponds roughly to a lattice volume $\frac{4}{3}\pi L^3$.

[3] This value corresponds roughly to the ratio of the electron and deuteron masses. Using this value emphasizes the fact that quantum triple collision states do exist even for small values of μ, in spite of the kinetic penalty associated to the small mass particle. For larger values of μ these states also exist, lower in the spectrum.

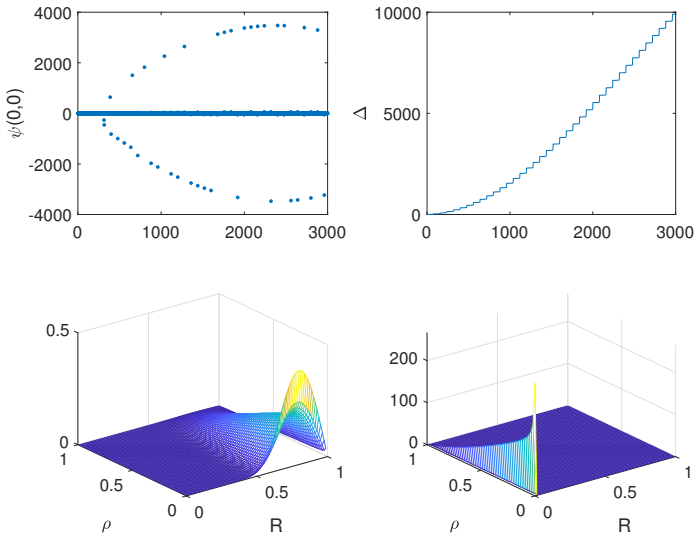

Figure 1: $\psi(0,0)$ for the first 3000 discretized eigenstates (40 energy levels), the energy difference Δ between the ground and the excited states (in H units) and the wave functions of the ground state (lower left panel) and the first quantum triple collision state (lower right panel)

respectively, the wave functions of the ground state ψ_0 and of the first quantum triple collision state ψ_1^*.

Because of the inhibiting effect of the Coulomb barrier between the two positively charged particles, it is expected that the QTC states will be relatively high in the spectrum and sparse, because many other, less exceptional, configurations would have similar energy. In particular, it is not to be expected that such states will occur spontaneously in a Coulomb system. Hence, the objective now is to assess the possibility to carry the system from the ground state ψ_0 to the state ψ_1^* by quantum control. The most effective way for coherently control the evolution of a quantum system is through the interaction with an electromagnetic field with a spectral content and temporal profile that may be altered throughout the process. The evolution equation would be

$$i\hbar\partial_t\psi(t) = (H - \epsilon(t) H_1)\psi(t) \tag{9}$$

where H is the original Hamiltonian, H_1 the control operator and $\epsilon(t)$ the time varying control intensity. A well established technique of optimal control [11] [12] [13] [14] [15] defines a function F , to be minimized, which contains both the objective goal and all the desired control constraints, among them the equation of motion (9). The constraints are made independent by the introduction of Lagrangian multiplier fields and the optimal control intensity $\epsilon(t)$ is obtained by iterative forward integration of (9) and backward integration of the Lagrange multiplier equations. This method allows for the introduction of arbitrary con-

trol constraints, in particular the fluency $\int \epsilon(t)^2 dt$ of the control field. In this setting open source codes have even been constructed to implement optimal quantum control [16] [17].

Optimal control methods are most appropriate an accurate equation of motion is known. This is so, of course, for the present simplified model and the methods of optimal control might readily be used. However, in a practical situation for a Coulomb system embedded on a molecular lattice, the crystal potentials of the lattice may preclude an exact knowledge of relevant equations. Therefore, it was preferred to emphasize a more direct control methodology, which is in fact closer to an experimental learning methodology. This is the local field approach, which defines a Lyapunov function [18] by the squared overlap of the current $\psi(t)$ and a target state ψ_1^*

$$M(t) = (\psi(t), \psi_1^*)(\psi_1^*, \psi(t)) \tag{10}$$

and chooses $\epsilon(t)$ during the evolution, with initial condition ψ_0, to insure that $\frac{d}{dt}M \geq 0$. Because

$$\frac{dM(t)}{dt} = -\epsilon(t)\frac{2}{\hbar} Im\{(\psi(t), \psi_1^*)(\psi_1^*, H_1\psi(t))\} \tag{11}$$

the condition $\frac{d}{dt}M \geq 0$ is satisfied if

$$\epsilon(t) = -\alpha Im\{(\psi(t), \psi_1^*)(\psi_1^*, H_1\psi(t))\} \tag{12}$$

α being a positive constant.

Even for a system contained in a box, the Hilbert space of solutions of the equation (9) is infinite-dimensional and it is known that full quantum controllability in infinite dimensions is a delicate problem [19] requiring non-Lie algebraic operators or approximations thereof [20] [21]. In this case however one deals with a simpler problem of controllability between two states in a discrete spectrum. It is known that in this case a necessary condition [22] is transitivity of the operator H_1. Hence the first thing to check is the availability of H_1 operators that are transitive between these two states, in the sense that there is an iteration H_1^n of the operator with non-vanishing matrix elements between the two states.

In the dipole approximation the interaction of the charged particles with the electric field of a laser pulse takes place through the dipole operator, namely

$$D = (R - \rho) \cdot E \tag{13}$$

with $Z = q = 1$, E the electrical field and all constants included in $\epsilon(t)$. To obtain the effect of this operator on the maximally symmetric states one integrates over all angles obtaining

$$H_1^{(E)} = \frac{1}{16R\rho}\left\{(R+\rho)^3 - |R-\rho|^3\right\} \tag{14}$$

The transitivity of this operator is found by computing $\left|\left(\psi_1^*, H_1^{(E)^n}\psi_0\right)\right|$ for successive powers of the operator. The result is shown in the left-hand panel

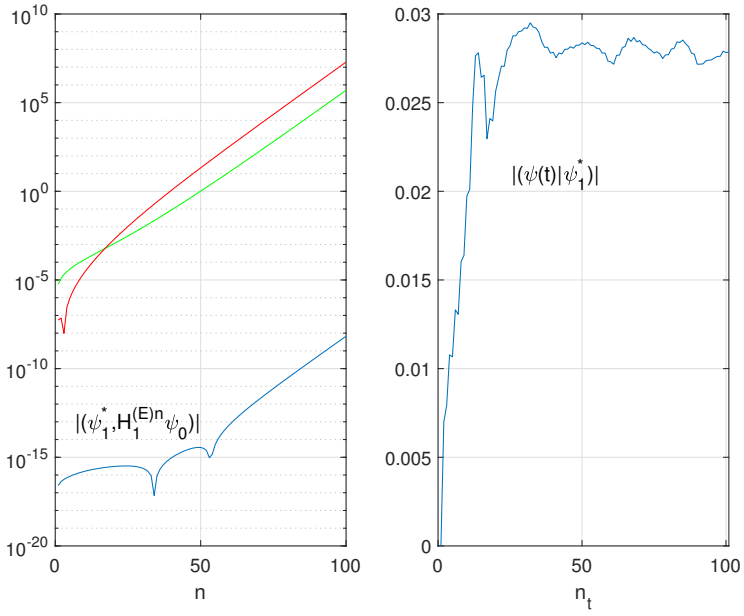

Figure 2: $\left|\left(\psi_1^*, H_1^{(E)^n}\psi_0\right)\right|$ compared with similar matrix elements replacing ψ_1^* by two states with $\psi(0,0)=0$ (left panel) and a control attempt with the dipole operator (right panel). n_t is the number of control steps with $dt=0.05$

of Fig.2 where this value is compared with the corresponding matrix element with ψ_1^*, the first QTC state, replaced by two other randomly chosen states for which $\psi(0,0)=0$. This shows that, starting from the ground state, the quantum triple collision state is not controllable with this operator. This is confirmed in the right-hand panel where a control attempt is made using the Lyapunov method and adjusting the field $\epsilon(t)$ intensity at each step by (12). The time step is $dt=0.05$ and the exponential of the operator is computed at every step to improve the precision. One sees that the overlap $|(\psi_0,\psi_1^*)|$ always remains at the level of the numerical round-off. The uncontrollability by the dipole operator is in fact to be expected because in the quantum triple collision state R and ρ are expected to be small, even for states that are not maximally symmetric. In the maximally symmetric case, studied here, one sees from Fig.1 that in the ψ_1^* state $R\approx 0$ and therefore the operator $H_1^{(E)}$ in (14) vanishes.

For a controlling alternative one considers the interaction with a magnetic field B. This interaction has two different terms, the paramagnetic and the diamagnetic, both arising from the substitution $p\to p-eA(x,t)$. The paramagnetic term may be written

$$-\frac{e}{2m}L\cdot B$$

and therefore, being proportional to the orbital angular momentum L, it vanishes for a maximally symmetric state. The diamagnetic term is proportional

to

$$\rho^2 \left(B_z^2 + B_y^2\right) + Z\mu R^2$$

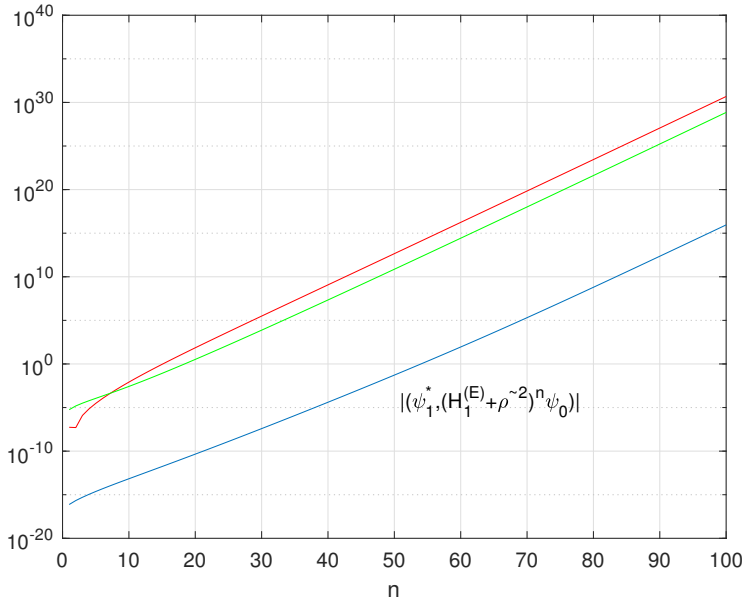

Figure 3: $\left|\left(\psi_1^*, \left(H_1^{(E)} + \rho^2\right)^n \psi_0\right)\right|$ compared with similar matrix elements replacing ψ_1^* by two states with $\psi(0,0) = 0$

If $M \gg m$, μ is very small and will be mostly the operator ρ^2 that might have a controlling effect. In Fig.3 one shows the successive values of $\left|\left(\psi_1^*, \left(H_1^{(E)} + \rho^2\right)^n \psi_0\right)\right|$. Ones sees that in this case the matrix element becomes large, although not so large as the corresponding matrix elements for the same two reference states as used in Fig.2 . Some degree of controllability is confirmed by using again the Lyapunov method now with the operator

$$H_1^{(M)} = H_1^{(E)} + \rho^2$$

The result of the numerical calculation is shown in Fig.4 where one sees that the overlap indeed grows rapidly on the first four iterations then settling around 12%. The left-hand panel shows the overlap $|(\psi(t), \psi_1^*)|$, the middle one the control intensity $\epsilon(t)$ and the right-hand panel the wave function $\psi(t)$ after 100 iterations. Although the controlled wave function is very close to a quantum triple collision situation, the overlap is still small because, as seen in right-hand panel, the overlap with the objective function is mostly in the region of small ρ and R where the integration measure (7) is small.

In conclusion: A Coulomb system of two positive and one negative charge confined in a box has quantum triple collision states. These states are high

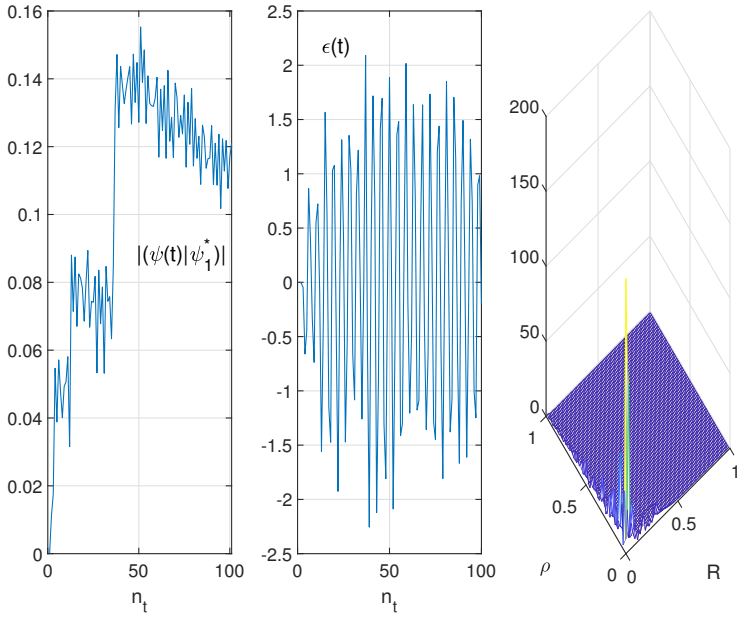

Figure 4: Control with the $H_1^{(M)}$ operator. The overlap $|(\psi(t), \psi_1^*)|$ (left panel), the control intensity $\epsilon(t)$ (central panel) and the wave function $\psi(t)$ after 100 iterations (right panel)

excited states in the spectrum. They are many but still exceptional in a "sea" of states with $\psi(0,0) = 0$. Quantum control from the ground state, by the dipole operator, is not possible in maximally symmetric states and also expected to be inefficient for non-symmetric states. However, it seems possible using time-varying magnetic fields. Magnetic control might even be more efficient for non-symmetric states because of the action of the paramagnetic term.

Notice however that the non-controllability result with the dipole operator and the electric field refers only to exact controllability, which arises from the non-transitivity of the $H_1^{(E)}$ operator. What one observes, for example in the control experiment reported in the right-hand panel of Fig.2, is that the controlled wave function $\psi(t)$ converges to states of close proximity (R small), nevertheless with negligible overlap with the objective function ψ_1^*.

In an actual 3-body Coulomb system confined in a solid lattice, accurate calculation of the energy levels will be difficult, because it is strongly influenced by the solid state environment. Therefore to have success in the use of quantum triple collisions to induce molecular or nuclear reactions, some automatic learning process as in [23] [24] is recommended. Another important consideration in any experimental implementation of this quantum control technique is the order of magnitude of the electromagnetic energies to be used. The normalized Hamiltonian H in Eq.(6) is a dimensionless quantity and to convert $H-$computed energy differences into physical values one should multiply them

by $\frac{Z^2 m e^4}{8\pi^2 \varepsilon_0^2 \hbar^2}$. Notice however that there is another dimensionless parameter that has to be taken into account. It is the ratio $\mu = \frac{m}{M}$ of the masses of the negative and the positively charged particles. As an illustration, for the μ values used in the numerical calculations that were performed, which correspond to ratios of the electron mass to typical nuclear masses, energy differences between the ground state and the first QTC states would be located in the high ultraviolet - low X-ray range. As for the intensity of the fields, it will strongly depend on the experimental setting, on the volume of the samples, on the absorption of the material, etc. and no safe implementation-independent estimate may be made.

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