

I. SIMULATION OF IONS IN A PENNING TRAP

Ions are confined radially by a magnetic field \mathbf{B} , with an ideal quadrupolar trapping potential of V_T . The potential and field near the centre of the trap is approximated as

$$\Phi_T(x, y, z) = V_T(\gamma' - \frac{\alpha'}{2l^2}(x^2 + y^2 - 2z^2)) \quad \mathbf{E} = -\nabla\Phi_T(x, y, z) = \frac{\alpha}{l^2}(-x\mathbf{i} - y\mathbf{j} + 2z\mathbf{k}) \quad (1)$$

where $\gamma' = 1/3$ and $\alpha' = 2.77373$ are geometric factors for the cubic trap, and l is the edge length[1]. The force experienced by an ion in the trap is

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (2)$$

Charges and mass are simulated in atomic units, lengths in nm and time in ns.

A. Integration scheme

The code uses the Boris integrator[2] as formulated in Birdsall and Langdon[3]. This is a modified leapfrog scheme in which positions are calculated at times $\dots, n-1, n, n+1, \dots$ and velocities at times $\dots, n^{-1/2}, n^{+1/2}, \dots$

$$\mathbf{v}^- = \mathbf{v}^{n-1/2} + \frac{q\mathbf{E}}{m} \frac{\Delta t}{2} \quad (3)$$

$$\mathbf{v}' = \mathbf{v}^- + \mathbf{v}^- \times \mathbf{t} \quad \mathbf{t} = \frac{q\mathbf{B}}{m} \frac{\Delta t}{2} \quad (4)$$

$$\mathbf{v}^+ = \mathbf{v}^- + \mathbf{v}' \times \mathbf{s} \quad \mathbf{s} = \frac{2\mathbf{t}}{1 + t^2} \quad (5)$$

$$\mathbf{v}^{n+1/2} = \mathbf{v}^+ + \frac{q\mathbf{E}}{m} \frac{\Delta t}{2} \quad (6)$$

B. Ion motion

The cyclotron frequency ω_c is predicted by $\omega_c = \frac{qB}{m}$ [1] (S.I. units - see Table III). To achieve 1% phase error in simulated cyclotron frequency requires $\Omega\Delta t \lesssim 0.3$ [3], [4]. The cyclotron radius r is predicted by $r = \frac{mv}{|q|B}$ and is measured in simulation for a single particle by the distance between maxima in the x dimension.

The electric field gives rise to a magnetron motion of a lower frequency ω_z . In a quadrupolar trapping potential of V_T , the modified cyclotron frequency ω_+ is predicted by

$$\omega_+ = \frac{\omega_c}{2} + \sqrt{\frac{\omega_c^2}{4} - \frac{\omega_z^2}{2}} \quad \omega_z = \left(\frac{2\alpha q V_T}{ml^2} \right)^{1/2} \quad (7)$$

The modified cyclotron frequency is measured by peaks in the Fourier transform of the induced current time signal.

C. Induced current

FTICR-MS measures the current induced between detector plates on opposite walls of the cube parallel to the magnetic field. In the simulation, current is induced by the movement of the 'image' $\mathbf{E}_{image}(\mathbf{r})$ associated with each ion, that is, the difference in the electric field generated by the ion at each of the two detector plates[1].

$$I = \sum_{i=1}^N q_i \mathbf{v}_i \cdot \mathbf{E}_{image}(\mathbf{r}_i) \quad \mathbf{E}_{image}(\mathbf{r}) = -\frac{\beta'}{l} r_j \quad \beta' = 0.72167 \quad (8)$$

D. Evaluation of electrostatic potential and forces

In addition to the influence of the trapping field and the ion-image interaction, each ion experiences a repulsive Coulomb force from every other ion in the packet. The calculation of these forces is nominally $O(N^2)$, which makes it infeasible for simulation of large ion packets unless some approximation is used to reduce the computational complexity. Previous simulations have either used the particle-in-cell approximation[5] or virtual particles to reduce the number of interactions to be simulated[6]. Particle-in-cell simulations are best suited to uniform particle distributions with a low required accuracy[7]. In contrast, the adaptive fast multipole algorithm[8] provides guaranteed error bounds for highly non-uniform distributions.

TABLE I
REPLICATING: HAN AND SHIN[9]. INPUT, PREDICTED AND MEASURED SIMULATION PARAMETERS

$B = 0.7646T, V_T = 1.0V, l = 0.047$												
species	charge	mass	v_0 (m/s)	predicted		measured		error: timestep				
				$\omega_+/2\Pi$ (Hz)	r (mm)	$\omega'_+/2\Pi$ (Hz)	r' (mm)	Δt (ns)	$\epsilon : \Delta t$	$\epsilon : \Delta t / 10$	$\epsilon : \Delta t * 10$	
HCO ⁺	1	29.0182	10 ⁴	394,022	3.933	404,220	3.933	118				
CH ₃ CO ⁺	1	43.04462	10 ⁴	262,028	5.835	272,460	5.835	175				

TABLE II
REPLICATING: LEACH ET AL.[5]. INPUT, PREDICTED AND MEASURED SIMULATION PARAMETERS

$B = 7.0T, V_T = 1.0V, l = 0.0508$												
species	charge	mass	v_0 (m/s)	predicted		measured		error: timestep				
				$\omega_+/2\Pi$ (Hz)	r (mm)	$\omega'_+/2\Pi$ (Hz)	r' (mm)	Δt (ns)	$\epsilon : \Delta t$	$\epsilon : \Delta t / 10$	$\epsilon : \Delta t * 10$	
Cs ⁺	1	132.9054	2.7×10^4	807,826	5.313	807,680	5.319	59				
Xx ⁺ ($\frac{m}{q} = 150$)	1	150.0	2.7×10^4	715,652	5.996	715,840	5.997	67				

E. Simulation results

REFERENCES

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TABLE III
CONVERSION FACTORS

property	unit	SI unit
mass	amu	$1.660538921 \times 10^{-27} kg$
charge	e	$1.60217653 \times 10^{-19} C$