

## 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  $\omega_c$  is predicted by  $\omega_c = \frac{qB}{m}$ [1]. 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 for a single particle simulation by the distance between maxima in the  $x$  dimension.

In a quadrupolar trapping potential of  $V_T$ , the modified cyclotron frequency  $\omega_+$  is predicted by

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

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 walls of the cube parallel to the magnetic field. In the simulation, current is induced by the movement of the 'image'  $\mathbf{E}_{image}(r)$  associated with each ion, that is, a charge equal in magnitude to the potential that would be produced at the ion position due to a unit potential applied to the detector electrode[1].

$$I = q\mathbf{v} \cdot \mathbf{E}_{image}(\mathbf{r}) \quad \mathbf{E}_{image} = -\frac{\beta'}{l} r_j \quad \beta' = 0.72167 \quad (8)$$

### D. Simulation results

TABLE I  
REPLICATING: HAN AND SHIN[5]. INPUT, PREDICTED AND MEASURED SIMULATION PARAMETERS

$B = 0.7646T, V_T = 0.0V, l = 0.047$ TODO rerun with $V_T = 1.0V$										
species	charge	mass	$v_0$ (m/s)	predicted		measured		error: timestep		
				$\omega_c/2\pi$ (Hz)	$r$ (nm)	$\omega'_c/2\pi$ (Hz)	$r'$ (nm)	$\Delta t$ (ns)	$\epsilon : \Delta t$	$\epsilon : \Delta t / 10$
HCO <sup>+</sup>	1	29.0182	10	404,618	3,933	404,531	3,933	118		
CH <sub>3</sub> CO <sup>+</sup>	1	43.04462	10	272,770	5,835	272,777	5,835	175		

TABLE II  
REPLICATING: LEACH ET AL.[6]. 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)	$r$ (nm)	$\omega'_+/2\Pi$ (Hz)	$r'$ (nm)	$\Delta t$ (ns)	$\epsilon : \Delta t$	$\epsilon : \Delta t / 10$	$\epsilon : \Delta t * 10$	
$\text{Cs}^+$	1	132.9	27	807,826	5,313	807,656	5,319	59				
$?(\frac{m}{q} = 150)$	1	150.0	27	715,654	5,996	715,781	5,997	67				

TABLE III  
CONVERSION FACTORS

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

## REFERENCES

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