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

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

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

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

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 $..., n-1, n, n+1, ...$ and velocities at times $..., n^{-1/2}, n^{+1/2}, ...$

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

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

$$\mathbf{v}^+ = \mathbf{v}^- + \mathbf{v}' \times \mathbf{s} \qquad \mathbf{s} = \frac{2\mathbf{t}}{1+t^2} \tag{5}$$

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

B. Ion motion

The cyclotron angular velocity ω_c is predicted by $\omega_c = \frac{qB}{m}$, with cyclotron frequency $\nu_c = \frac{\omega_c}{2\Pi}$[1] (S.I. units - see Table V). To achieve 1% phase error in simulated cyclotron frequency requires $\omega\Delta t \lesssim 0.3$[3], [4].

Ions are excited to a uniform radius r, with different velocities and kinetic energies. The magnitude of ion velocity in the xy plane is predicted by $v_{xy} = \frac{qBr}{m}$ (S.I. units).

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

$$\omega_+ = \frac{\omega_c}{2} + \sqrt{\frac{\omega_c^2}{4} - \frac{\omega_z^2}{2}} \qquad \omega_z = \sqrt{\frac{2\alpha q V_T}{ml^2}} \tag{7}$$

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

C. Induced current

In experiment, the current is measured 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].

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

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 the simulation of large ion packets infeasible unless some approximation is used to reduce the computational complexity.

Ion excitation and detection is typically performed in a vacuum, or in an environment of low-pressure neutral gas particles. To produce a detectable ICR signal, it is necessary to excite the ions so as to produce a highly coherent circular motion. Thus the distribution of charged particles within the FT-ICR chamber is highly non-uniform. Previous simulations have either used the particle-in-cell approximation[5] or virtual particles to reduce the number of interactions to be simulated[6]. However, 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 non-uniform distributions.

E. Fast multipole algorithm

The cubic simulation space is divided into an octree of s levels according to a desired mean number of particles per lowest level box N_0 such that $s = \lceil log_8(N/N_0) \rceil$. The side length of a *leaf* box at the lowest level is therefore $a/8^s$. Tree parameters are given for sample problem sizes where $N_0 = 100$ in table I-E.

N	**s**	**leaf box size** (m)
10^4	3	1.95×10^{-6}
10^5	4	2.44×10^{-7}
10^6	5	3.10×10^{-8}

TABLE I
OCTREE PARAMETERS, $N_0 = 100$

F. Replication of previously published simulation results

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

$B = 0.7646T, V_T = 1.0V, l = 0.047, \Delta t = 25ns$										
				predicted		**measured**	**error: timestep**			
species	**charge**	**mass**	r **(mm)**	ν_+ **(Hz)**	v_0 **(m/s)**	ν'_+ **(Hz)**	Δt **(ns)**	$\epsilon : \Delta t$	$\epsilon : \Delta t$ **/ 10**	$\epsilon : \Delta t$ *** 10**
HCO^+	1	29.0182	5.0	404,356	1.27×10^4	404,220	118			
CH_3CO^+	1	43.04462	5.0	272,508	8.57×10^3	272,460	175			

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

$B = 7.0T, V_T = 1.0V, l = 0.0508, \Delta t = 25ns$										
				predicted		**measured**	**error: timestep**			
species	**charge**	**mass**	r **(mm)**	ν_+ **(Hz)**	v_0 **(m/s)**	ν'_+ **(Hz)**	Δt **(ns)**	$\epsilon : \Delta t$	$\epsilon : \Delta t$ **/ 10**	$\epsilon : \Delta t$ *** 10**
Cs^+	1	132.9054	6.0	808,767	2.70×10^4	807,680	59			
$Xx^+(\frac{m}{q} = 150)$	1	150.0	6.0	716,594	3.05×10^4	715,840	67			

G. Comparison with experiment: amino acids

We performed a scan of a mixture of lysine and glutamine on a Bruker Apex 4.7T FT-ICR mass spectrometer at the ANU. The core of this machine is a Penning trap of 4.7T / 1.0V of side length 1cm. We performed a molecular dynamics simulation for an equimolar mixture of N singly-charged ions in total. The simulation parameters and results are in table IV.

TABLE IV
AMINO ACIDS IN ANU MASS SPECTROMETER. INPUT, PREDICTED AND MEASURED SIMULATION PARAMETERS

$B = 4.7T, V_T = 1.0V, l = 0.01, \Delta t = 25ns$										
				predicted		**measured**	**error: timestep**			
species	**charge**	**mass**	r **(mm)**	v_0 **(m/s)**	ν_+ **(Hz)**	ν'_+ **(Hz)**	Δt **(ns)**	$\epsilon : \Delta t$	$\epsilon : \Delta t$ **/ 10**	$\epsilon : \Delta t$ *** 10**
glutamine	1	147.07698	3.0	9.25×10^3	489,779	489,540	106			
lysine	1	147.11336	3.0	9.25×10^3	489,658	489,407	106			

H. Peak coalescence

Vladimirov et al.[10] give an expression for the minimum number of ions required for coalescence of two clouds of (singly-charged) ions of similar masses m_1 and m_2:

$$N = 4.87 \times 10^8 \frac{a^2 R B^2 (m_2 - m_1)}{m^2} \tag{9}$$

(For a, R in mm, m_1, m_2, m in Da, B in Tesla.)

Applying this formula to the experiment described in section I-G, where ion cloud major axis $a \approx 1$ mm, ion cyclotron radius $R \approx 3$ mm, and average mass $m = 147.09517$, we find the minimum number of ions required for coalescence is ≈ 55000.

TABLE V
CONVERSION FACTORS

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

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