Original Investigations

Collisionally Damped Ion Motion in ICR Spectrometry

Hermann Hartmann, Kyu-Myung Chung, Dieter Schuch and Jürgen Radtke

Institut für Physikalische und Theoretische Chemie der Johann-Wolfgang-Goethe Universität, Robert-Mayer-Str. 11, D-6000 Frankfurt (Main), Federal Republic of Germany

A Schrödinger equation equivalent to the Langevin equation of ion motion in ICR cells is presented. A wave function for the scattering states has been found as the solution to the equation of ion motion under the influence of electric and magnetic fields perturbed by a scattering potential. Applying the minimized wave packet as a wave function describing coherent states, the scattering amplitudes are determined explicitly. The connection between the collision cross section and the scattering amplitudes is found by making use of the incoming and outgoing particle flux density. The collision cross section found in this way is converted from quantum theory to classical physics. The collision cross section, which plays an essential role in the determination of rate constants can be determined by the aid of ICR experimental data if the contribution of an alternating electric field is taken into account.

Key words: Ion cyclotron resonance spectrometry – Collisionally damped ion motion in ICR spectrometry

1. Introduction

The motion of ions under the influence of electric and magnetic fields can be well described by classical physics. Many authors [1–4] have contributed the essentials applying classical physics to this field, for instance the determination of rate constants of ions in the gas phase by measuring the halfwidths of ICR spectral lines. In spite of the fact that the results agree well with the measurements, the applied classical theories conceal certain difficulties. With regard to this point, we may remind of the collision frequencies and the scattering cross sections obtained classically. These quantities can not be determined rigorously within the scope of classical physics. Despite this difficulty, one will be compelled to accept some lack

of exactness in the theory, for example in the case of the impact parameters, if one dares to determine such quantities theoretically. Another possible means for the treatment of ions in the gas phase is quantum theory. But one may think that a quantum mechanical treatment is unnecessary because the ions behave practically like classical particles in the gas phase. We agree entirely with those who refuse to apply pure quantum states as these are quite different from the classical states [16]. Nevertheless we argue that coherent states which consist of infinitely many pure quantum states can be applied to the classical problem. Hartmann and Chung [5] have used the minimized wave packet as a wave function for such coherent states to describe the ICR power absorption. In another paper, Hartmann and Chung have furthermore shown in which way such quantum theoretical results can be converted to classical ones [6].

The cyclic course we are going here, starting off from the classical formulation of the problem and returning to classical physics again after a quantum theoretical excursion, still has a gap inasmuch as the quantum mechanical formulation of the problem has not been deduced so far on the basis of the classical formulation. We now close this circle by bridging the gap. This may be done by the aid of the methods developed by Madelung and Mrowka [7, 8], who use three principles as axioms in their representation theory of quantum mechanics, namely:

1) Heisenberg's uncertainty principle or complementarity,
2) the fact that interference phenomena show up in experiments with material systems and
3) correspondence principle or Ehrenfest's theorem.

The aim of this work is to pursue the cyclic course, starting from the well established classical theory, proceeding by a quantum mechanical excursion to evaluate the results, and returning to classical theory again by a conversion of the results obtained quantum theoretically to the corresponding classical expression. As an example, we shall treat the Langevin equation of ion motion in the ICR cell which will be represented by the corresponding Schrödinger equation. The solution of the equation turns out to be a solution of scattering states from which we obtain the scattering cross section. This cross section will be converted to the classical expression which can be applied to determine the rate constants.

2. The Wave Equation Equivalent to the Langevin Equation

The motion of an ion undergoing collisions with the background neutrals in ICR cells can best be described classically by the Langevin equation

$$m\dot{v} = eE + \frac{e}{c}(v \times H) - m\Gamma v \tag{1}$$

where Γ is the damping parameter, E the electric field, and H the magnetic field. To obtain the Schrödinger equation equivalent to the Langevin equation (1), we

apply the methods of Madelung and Mrowka. The force acting on the ion is given by

$$K = e\left\{-\operatorname{grad} \Phi - \frac{1}{c}\frac{\partial A}{\partial t} + \frac{1}{c}(v \times \operatorname{rot} A)\right\} - m\Gamma\dot{r}. \tag{2}$$

Assuming that the distribution function ρ is a bilinear form

$$\rho = \alpha\cdot\beta \geqslant 0 \tag{3}$$

with the probability amplitudes $\alpha(r, t)$ and $\beta(r, t)$, and where the statistical current density of the representation points is given by

$$j = C\{\beta \operatorname{grad} \alpha - \alpha \operatorname{grad} \beta\} - a\alpha\beta, \tag{4}$$

we obtain by the aid of the continuity equation

$$\dot{\rho} + \operatorname{div} j = 0 \tag{5}$$

the differential equation

$$\dot{\alpha} + C\,\Delta\alpha - \frac{\alpha}{2}\operatorname{div} a - (a\cdot\operatorname{grad}\alpha) + f\alpha = 0; \tag{6}$$

and with $\rho = \alpha\beta; j = \rho v$ we get

$$m\frac{\overline{dv}}{dt} = m\int \frac{\partial j}{\partial t}\,d\tau = m\int \rho\left\{-\operatorname{grad}\left(2Cf - \frac{a^2}{2}\right) - \frac{\partial a}{\partial t} + (v \times \operatorname{rot} a)\right\}d\tau.$$

Comparison with

$$\overline{K} = e\int \rho\left\{-\operatorname{grad}\Phi - \frac{1}{c}\frac{\partial A}{\partial t} - m\Gamma v + \left(\frac{v}{c} \times \operatorname{rot} A\right)\right\}d\tau$$

shows that the relations

$$m\frac{\partial a}{\partial t} = \frac{e}{c}\frac{\partial A}{\partial t} + m\Gamma v \tag{7}$$

$$2Cmf - \frac{m}{2}a^2 = e\Phi$$

should be satisfied.

We make use of the fact that the Schrödinger equation is invariant under a gauge transformation of the potentials accompanied by a unitary phase transformation of the wave functions:

$$\hat{A} = A + \operatorname{grad}\hat{F}; \qquad \hat{\Phi} = \Phi - \frac{1}{c}\frac{\partial\hat{F}}{\partial t} \tag{8}$$

$$\hat{\Psi} = \exp\left(\frac{ie}{\hbar c}\hat{F}\right)\cdot\overline{\Psi}.$$

With this gauge transformation, utilizing the first equation of (7) we can choose the function $\hat{F}$ to fulfill

$$\frac{e}{mc} \operatorname{grad} \hat{F} + \Gamma r = 0, \tag{9}$$

so that the solution of the first equation yields

$$a = \frac{e}{mc} A. \tag{10}$$

Integrating Eq. (9) we obtain

$$\hat{F} = -\frac{mc}{2e} \Gamma r^2 + g(t) \tag{11}$$

where $g(t)$ is a function of time alone.

With the identifications $\alpha = e^{(ie/\hbar c)\hat{F}} \cdot \overline{\Psi}$; $C = \hbar/2mi$ the differential equation (6) multiplied by the factor $\hbar/i$, turns out to be

$$\left[\frac{\hbar}{i} \frac{\partial}{\partial t} - \frac{\hbar^2}{2m} \nabla^2 - \frac{\hbar e}{2imc} \operatorname{div} A - \frac{\hbar e}{imc} (A \cdot \operatorname{grad}) + \frac{e^2}{2mc^2} A^2 + e\Phi - \frac{e}{c} \dot{g}(t) \right]$$
$$\cdot e^{(ie/\hbar c)\hat{F}} \cdot \overline{\Psi} = 0. \tag{12}$$

Assigning $[\Omega - (e/c)\dot{g}]$ to the operator in Eq. (12) and multiplying by

$$\exp\left[(-ie/\hbar c)\hat{F}^*\right]$$

from the left, we can express the Schrödinger equation (12) as

$$e^{(-ie/\hbar c)\hat{F}^*}\left[\Omega - \frac{e}{c} \dot{g} \right] e^{(ie/\hbar c)\hat{F}}\overline{\Psi} = \tilde{\Omega}\overline{\Psi} = 0. \tag{13}$$

Because of the symmetric gauge of the vector potential $A = \frac{1}{2}(H \times r)$ the relation $(A \cdot r) = 0$ is valid and the operator $\tilde{\Omega}$ assumes the form

$$\tilde{\Omega} = \Omega + \frac{m}{2} \Gamma^2 r^2 + \frac{i\hbar}{2} \Gamma. \tag{14}$$

Using the transformation $\hat{S} = e^{(\Gamma/2)t}$ Eq. (13) can be converted to

$$\hat{S}^{-1}\tilde{\Omega}\hat{S}\hat{S}^{-1}\overline{\Psi} = \left(\Omega + \frac{m}{2} \Gamma^2 r^2 \right) [e^{(-\Gamma/2)t} \cdot \overline{\Psi}] = \left(\Omega + \frac{m}{2} \Gamma^2 r^2 \right)\Psi = 0. \tag{15}$$

The Schrödinger equation equivalent to the Langevin equation of motion (1) is therefore given by

$$\left\{ \frac{1}{2m} \left(\frac{\hbar}{i} \nabla - \frac{e}{c} A \right)^2 + e\Phi + T \right\} \cdot [e^{(-\Gamma/2)t} \cdot \overline{\Psi}] = i\hbar \frac{\partial}{\partial t} [e^{(-\Gamma/2)t} \cdot \overline{\Psi}]. \tag{15a}$$

In this equation the wave function $\Psi = e^{(-\Gamma/2)t} \cdot \overline{\Psi}$ contains the damping factor $e^{(-\Gamma/2)t}$ and the additional energy $T = (m/2)\Gamma^2 r^2$ occurs; both of them are due to the damping term in the Langevin equation.

3. The Scattering States of Ions

To describe the effects of the scattering potential T on the ion motion in the homogeneous fields, T should be regarded as a small perturbation. The problem therefore is to solve the equation $\Omega\Psi = -T\Psi$. Because of the separable form of the scattering potential $T = T_\perp + T_\parallel$ together with the decoupling of the electric potentials by the parametrization $e\Phi_\parallel = e\Phi_\parallel(\langle r_\perp\rangle, z)$ and $e\Phi_\perp = e\Phi_\perp(r_\perp, \langle z\rangle)$[9], the motion can be treated by the product ansatz $\Psi = \Psi_\perp \cdot \Psi_\parallel$ for the wave function.

The wave function for the ion motion in the magnetic field direction obeys the wave equation

$$\left\{\frac{\hbar}{i}\frac{\partial}{\partial t} - \frac{\hbar^2}{2m}\frac{d^2}{dz^2} + e\Phi_\parallel(\langle r_\perp\rangle, z)\right\}\Psi_\parallel(z, t) = -T_\parallel\Psi_\parallel(z, t). \tag{16}$$

By the aid of the Green function which satisfies the equation

$$\left\{\frac{\hbar}{i}\frac{\partial}{\partial t} - \frac{\hbar^2}{2m}\frac{d^2}{dz^2} + \langle e\Phi_\parallel\rangle\right\}G_\parallel(z - z', t - t') = -\delta(z - z')\cdot\delta(t - t') \tag{17}$$

the general solution of Eq. (16) may be written in the form

$$\Psi_\parallel(z, t) = \varphi_\parallel(z, t) + \int_{-\infty}^{+\infty} dz' \int_0^\infty d\tau G_\parallel(Z, \tau)T_\parallel\varphi_\parallel(z', t'), \tag{18}$$

where $Z = z - z'$, $\tau = t - t'$ and $\varphi_\parallel(z, t)$ is a solution of Eq. (16) in the homogeneous case. Green's function $G(Z, \tau)$, which satisfies Eq. (17), is given by

$$G_\parallel(Z, \tau) = \tfrac{1}{2}e^{i(\pi/4)}\left(\frac{2m}{\pi\hbar^3}\right)^{1/2}\frac{1}{\tau^{1/2}}\cdot\exp\left\{\frac{i}{\hbar}\left[-\langle e\Phi_\parallel\rangle\tau + \frac{m}{2}\frac{Z^2}{\tau}\right]\right\}\cdot\Theta(\tau) \tag{19}$$

where $\Theta(\tau)$ is the Heaviside function.

Carrying out the time integration in Eq. (18) inserting expression (19) for $G_\parallel(Z, \tau)$, we obtain

$$\tilde{G}_\parallel(Z) = \int_0^\infty d\tau G_\parallel(Z, \tau)\cdot\exp\left[-(i/\hbar)E_\parallel^0 t'\right]$$

$$= i\frac{m}{\hbar^2 K_\parallel}\cdot\exp\left(iK_\parallel Z - \frac{i}{\hbar}E_\parallel^0 t\right) \tag{20}$$

where

$$K_\parallel = \left[\frac{2m}{\hbar^2}(E_\parallel^0 - \langle e\Phi_\parallel\rangle)\right]^{1/2} \quad\text{and}\quad E_\parallel^0 = (n + \tfrac{1}{2})\hbar\omega_t.$$

The solution for the scattering states can be expressed as

$$\Psi_\parallel(z, t) = \varphi_\parallel(z, t) + \exp\left(iK_\parallel z - \frac{i}{\hbar}E_\parallel^0 t\right)\cdot\sum_i \langle\tilde{g}_\parallel t|\varphi_{\parallel i}\rangle\langle\varphi_{\parallel i}|T_\parallel|\varphi_\parallel\rangle \tag{21}$$

with

$$|\tilde{g}_\parallel\rangle = -\frac{im}{\hbar^2 K_\parallel}\exp(iK_\parallel z') \quad\text{and}\quad \sum_i |\varphi_{\parallel i}\rangle\langle\varphi_{\parallel i}| = 1.$$

Wave function (21) constitutes a linear harmonic oscillator function plus a propagating plane wave.

Taking $T_\perp = (m/2)\Gamma^2 r^2$ as a perturbation we can write the general solution for the wave function $\Psi_\perp(r_\perp, t)$ with the Green function for this problem

$$G_\perp(R_\perp, \tau) = \frac{m}{2\pi\hbar^2} \cdot \exp\left[\frac{ie}{\hbar c}(A(r'_\perp) \cdot R_\perp)\right] \cdot \frac{1}{\tau} \cdot \exp\left\{\frac{i}{\hbar}\left[-\langle e\Phi_\perp\rangle \tau + \frac{m}{2}\frac{R_\perp^2}{\tau}\right]\right\} \cdot \Theta(\tau) \tag{22}$$

as

$$\Psi_\perp(r_\perp, t) = \varphi_\perp(r_\perp, t) + \int d^2 r'_\perp \int dt' G_\perp(R_\perp, \tau) T_\perp \varphi_\perp(r'_\perp, t') \tag{23}$$

where $\varphi_\perp(r_\perp, t) = \bar{\varphi}_\perp(r_\perp, t) \cdot e^{-(\Gamma/2t)}$. The function $\varphi_\perp(r_\perp, t)$ is the solution of the Schrödinger equation for this problem without the perturbation [10].

The time integration can be carried out exactly and yields

$$\tilde{G}_\perp(R_\perp) = \int_0^\infty d\tau G_\perp(R_\perp, \tau) \cdot \exp\left(-\frac{i}{\hbar}E_\perp^0 t'\right)$$

$$= \frac{m}{2\pi\hbar^2} \exp\left\{\frac{i}{\hbar}\left[\frac{e}{c}(A_\perp(r'_\perp) \cdot R_\perp) - E_\perp^0 t\right]\right\} \cdot i\pi \, H_0^1(K_\perp R_\perp) \tag{24}$$

with

$$K_\perp = \left\{\frac{2m}{\hbar^2}(E_\perp^0 - \langle e\Phi_\perp\rangle)\right\}^{1/2} \quad \text{and} \quad E_\perp^0 = \frac{m}{2}\omega_c^2 R_c^2 - \frac{eE_D}{2}y_M + \frac{m}{2}w^2.$$

As the Hankel functions H_0^1 are particularly suited for the description of damped oscillations [11], expression (24) reflects the character of the motion due to collision correctly. Because the damping effect is large only near the scattering center, the dominant contribution to the integral with regard to $r'_\perp$ in Eq. (23) comes from the region $r'_\perp \ll r_\perp$. As we need the solution at large distances $r_\perp$ we replace the Hankel function by its asymptotic expression

$$i\pi H_0^1 \sim \sqrt{\frac{2\pi}{K_\perp}} \cdot e^{i(\pi/4)} \cdot R_\perp^{-1/2} \cdot \exp(iK_\perp R_\perp)$$

which is valid for $K_\perp R_\perp \gg 0$ and $K_\perp R_\perp > 1$.

Moreover, when using the approximation $R_\perp = r_\perp - (r_\perp \cdot r'_\perp)/r_{\perp'}$ the wave function $\Psi_\perp(r_\perp, t)$ can be written as

$$\Psi_\perp(r_\perp, t) = \varphi_\perp(r_\perp, t) + r_\perp^{-1/2} \cdot \exp\left(iK_\perp r_\perp - \frac{i}{\hbar}E_\perp^0\right) \cdot \sum_{N'} \langle \tilde{g}_\perp | \varphi_{\perp, N'}\rangle \langle \varphi_{\perp, N'} | T_\perp | \varphi_\perp\rangle \tag{25}$$

with

$$|\tilde{g}_\perp\rangle = \frac{m}{2\pi\hbar^2} e^{-i(\pi/4)}\left(\frac{2\pi}{K_\perp}\right)^{1/2} \cdot \exp\left\{\frac{-ie}{\hbar c}(A_\perp(r'_\perp) \cdot R_\perp) - iK_\perp r'_\perp \cos\Theta\right\}. \tag{26}$$

The wave function $\Psi_\perp$ consists of a phase-transformed screw function and an outgoing cylindrical wave with damped amplitude. The matrix elements and integrals which appear in expressions (21) and (25) can exactly be evaluated with the pure quantum state wave functions. As we are interested in the classical behavior we intend to evaluate these quantities by applying coherent states.

4. The Minimized Wave Packet as a Coherent State

A suitable means to describe classical ion motions in quantum theory is a wave packet constructed of infinitely many pure quantum state wave functions and minimized according to the uncertainty principle. The trapping motion of ions in the direction of the magnetic field can be described by the wave functions of the linear harmonic oscillator. Hartmann *et al.* [9] have applied such wave packets to solve the problem of the exact mass determination. The minimized wave packet is given by

$$\tilde{\varphi}_\parallel(z, t) = \left(\frac{\alpha}{\sqrt{2\pi}}\right)^{1/2} \cdot \exp\left\{-\frac{\alpha^2}{4}(z - a_z(t))^2\right\} \cdot \exp\left(-\frac{i}{2}\omega_t t\right)$$

$$= \sum_n p_n u_n(\alpha z) \cdot \exp\left\{-\frac{i}{\hbar}(n + \tfrac{1}{2})\hbar\omega_t t\right\}$$

(27)

with the weight function

$$p_n = (2^n \sqrt{n!})^{-1} \cdot \exp\left(-\frac{\alpha^2}{8} a_z^2\right) \cdot (\alpha a_z)^n$$

and

$$u_n(\alpha z) = \left(\frac{\alpha}{\sqrt{2\pi}\, n!}\right)^{1/2} \cdot \exp\left(-\frac{\alpha^2}{4} z^2\right) H_n(\alpha z) \quad \text{with} \quad \alpha = \left(\frac{mK}{\hbar^2}\right)^{1/4}.$$

Applying this wave packet solution (27), the integral in Eq. (21) shows the result

$$\langle \tilde{g}_\parallel | \tilde{\varphi}_\parallel \rangle = i\sqrt{2}\, \frac{m}{\hbar^2 K_\parallel}\, \frac{1}{\sqrt{\alpha}}\, (2\pi)^{1/4} \cdot \exp\left(-\frac{K_\parallel^2}{\alpha^2} - iK_\parallel a_z\right) \cdot \exp\left(-\frac{i}{2}\omega_t t\right).$$

(28)

The matrix element $\langle \tilde{\varphi}_\parallel | T_\parallel | \tilde{\varphi}_\parallel \rangle$ according to Eq. (21) can also be evaluated and converted making use of the relations

$$\sum_n p_n^* p_n = 1 \quad \text{and} \quad (n + \tfrac{1}{2})\hbar\omega_t = \frac{m}{2}\omega_t^2 b_t^2,$$

(29)

to the classical quantity

$$\langle \tilde{\varphi}_\parallel | T_\parallel | \tilde{\varphi}_\parallel \rangle = m\Gamma^2 b_t^2 = 2E_{\parallel\,\text{coll}}.$$

(30)

Introducing the collision wave number $K_{\parallel\,\text{coll}} = [(2m/\hbar^2)E_{\parallel\,\text{coll}}]^{1/2}$ and considering Eqs. (28) and (30), the wave packet solution can be expressed as

$$\tilde{\Psi}_\parallel(z, t) = \tilde{\varphi}_\parallel(z, t) + f(\gamma_\parallel, \delta_\parallel, K_\parallel) \cdot \exp\left(iK_\parallel z - \frac{i}{\hbar} E_\parallel^0 t\right)$$

(31)

with the scattering amplitude

$$f(\gamma_\parallel, \delta_\parallel, K_\parallel) = i(2\pi)^{1/4}\gamma_\parallel^2 \delta_\parallel^{1/2}\sqrt{2K_\parallel}\, \exp\left(-\delta_\parallel^2 - iK_\parallel a_z\right),$$

(32)

where

$$\gamma_\parallel = K_{\parallel\,\text{coll}}/K_\parallel, \qquad \delta_\parallel = K_\parallel/B_t \quad \text{and} \quad B_t = \sqrt{\frac{K_t}{b_t}}.$$

As $K_\| = (\pi/2)K_t$, $\delta_\|$ turns out to be $\sqrt{2\pi}/4$. Thus the scattering amplitude is completely expressed by classical quantities. Moreover it has the dimension of $(\text{length})^{-1/2}$ as a one-dimensional plane wave should have and rapidly vanishes at large distances from the scattering center. The solution (31) thus contains a typical scattering state that appears as a consequence of a collisionally caused damping term in the Langevin equation.

To describe the motion of ions in the plane perpendicular to the magnetic field in a drift ICR cell we can also construct a minimized wave packet using infinitely many phase-transformed screw functions and obtain

$$\tilde\varphi_\perp = \left(\frac{b}{2\pi}\right)^{1/2}\cdot\exp\left\{\frac{i}{\hbar}m[w\cdot(\rho - a(t))] + \frac{ie}{\hbar c}[A(r_m)\cdot(\rho - a(t))]\right.$$

$$\left. - \frac{b}{4}(\rho - a(t))^2 + \frac{i}{\hbar}mwx_m - \frac{i}{2}\omega_c t\right\} \tag{33}$$

$$= \sum_N p_N u_N(\rho)\cdot\exp\left\{-\frac{i}{\hbar}(N + \tfrac{1}{2})\hbar\omega_c t\right\}; \quad \rho = r_\perp - r_m$$

with the weight function

$$p_N = \frac{1}{\sqrt{N!e}}\cdot e^{iN[\alpha + 1/2]}J_N\left(\kappa\sqrt{\frac{2}{b}}\right); \quad \kappa = \frac{b}{2|r_m|}.$$

The phase-transformed screw function is given by [10]

$$u_N(\rho) = \left(\frac{b}{2\pi}\left(\frac{b}{2}\right)^N\frac{1}{N!}\right)^{1/2}\cdot\exp\left\{\frac{i}{\hbar}m(w\cdot r_\perp) + \frac{ie}{\hbar c}(A(r_m)\cdot r_\perp)\right\}$$

$$\cdot\exp\left[-\frac{b}{4}(r_\perp - r_m)^2\right]\cdot|r - r_m|^N\cdot\exp(-iN\varphi) \tag{34}$$

with $b = eB/\hbar c$ and the drift velocity $|w| = w = c(E_D/B)$. By the aid of this wave packet (33) the integral $\langle\tilde g_\perp|\tilde\varphi_\perp\rangle$ acc. to Eq. (25) can exactly be evaluated as [12]

$$\langle\tilde g_\perp|\tilde\varphi_\perp\rangle = \frac{m}{2\pi\hbar^2}e^{i(\pi/4)}\sqrt{\frac{2\pi}{K_\perp}}$$

$$\cdot\exp\left\{\frac{im}{\hbar}w(r'_m - a) + \frac{ie}{\hbar c}(A(r'_m)\cdot(r_\perp - a)) + iK_\perp r'_m\cos\Theta\right\}\cdot(2\pi b)^{1/2}\cdot I_\rho$$

with   (35)

$$I_\rho = \int_0^\infty J_0\left(\frac{b}{2}\rho|\tilde r|\right)\cdot\exp\left\{iK_\perp\rho\cos\Theta - \frac{b}{4}(\rho - a)^2\right\}\cdot\rho\,d\rho$$

$$= \frac{1}{2}\frac{1}{\sqrt{b|\tilde r|}}\left(\frac{2}{b}\right)^{3/4}\cdot\exp\left\{-\frac{b}{4}a^2 + \frac{p^2}{2b} - \frac{b}{8}|\tilde r|^2\right\}$$

$$\cdot\left[D_{-3/2}(Z_-)\cdot\exp\left(-\frac{i}{2}|\tilde r|p - i\frac{\pi}{4}\right) + D_{-3/2}(Z_+)\cdot\exp\left(\frac{i}{2}|\tilde r|p + i\frac{\pi}{4}\right)\right]$$

where $D_{-3/2}(Z_\pm)$ are parabolic cylinder functions of the arguments

$$Z_\pm = \sqrt{\frac{2}{b}} \left(p \pm \frac{i}{2} b|\tilde{r}| \right)$$

with the abbreviations

$$p = -\frac{b}{2} a - iK_\perp \cos \Theta \quad \text{and} \quad |\tilde{r}| = \left(x - x'_m, y - y'_m + \frac{2}{b} \frac{mw}{\hbar} \right).$$

Because the scattering states of ions under ICR experimental conditions satisfy $|Z_\pm| \gg 1$, $|\nu| = 3/2$ and $|\arg Z_\pm| < \frac{3}{4}\pi$, we can apply the asymptotic approximation $D_\nu(Z) \approx Z^\nu \cdot \exp(-Z^2/4)$. The integral I_ρ in Eq. (35) reduces to

$$I_\rho \approx \frac{e^{(-b/4)a^2}}{b^2|\tilde{r}|^2} \cdot 2^{3/2} \cdot \frac{3}{2} \cdot \left(-\frac{a}{|\tilde{r}|} - i \frac{2K_\perp \cos \Theta}{b|\tilde{r}|} \right). \tag{36}$$

The matrix element $\langle \tilde{\varphi}_\perp | T_\perp | \tilde{\varphi}_\perp \rangle$ according to Eq. (25) can exactly be evaluated applying the wave packet solution (33). We convert the matrix element by the aid of the relations $\sum_N p_N^* p_N = 1$ and $(N + \frac{1}{2})\hbar\omega_c = (m/2)\omega_c^2 R_c^2$ to the classical expression in which neither the quantum number N nor Planck's constant h appears:

$$\langle \tilde{\varphi}_\perp | T_\perp | \tilde{\varphi}_\perp \rangle = \frac{m}{2} \Gamma^2 (R_c^2 + r_m'^2) = E_{\perp \text{coll}}. \tag{37}$$

The scattering state solution (25) therefore becomes

$$\Psi_\perp = \tilde{\varphi}_\perp(r_\perp, t; r_m) + \frac{e^{iK_\perp r_\perp}}{r_\perp}$$

$$\cdot \exp \left\{ \frac{im}{\hbar} [w \cdot (r_m' - a)] + \frac{ie}{\hbar c} [A(r_m') \cdot (r_\perp - a)] - \frac{i}{\hbar} E_\perp^0 t \right\} \cdot f(\Theta) \tag{38}$$

with the scattering amplitude

$$f(\Theta) = e^{-i(\pi/4)} \cdot \frac{3}{4} \cdot \gamma_\perp^2 \delta_\perp^{5/2} \cos \Theta \cdot \exp (iK_\perp r_m' \cos \Theta) \tag{39}$$

for which we have applied the approximation of vanishing deviation $a \to 0$ and $|\tilde{r}| \to |r_\perp|$. We have assigned the abbreviations

$$\gamma_\perp = \frac{K_{\perp \text{coll}}}{K_\perp} = \left(\frac{E_{\perp \text{coll}}}{E_\perp^0 - \langle e\Phi_\perp \rangle} \right)^{1/2}$$

and

$$\delta_\perp = \frac{2K_\perp}{b\langle |r_\perp| \rangle} = 2 \left(\frac{2(E_\perp^0 - \langle e\Phi_\perp \rangle)}{m\omega_c^2 R_c^2} \right)^{1/2} = 2 \left(\frac{E_\perp^0 - \langle e\Phi_\perp \rangle}{\frac{1}{2}k_B T} \right)^{1/2} \tag{40}$$

and used the common estimation for the rotational energy

$$\frac{m}{2} \omega_c^2 R_c^2 = \frac{1}{2}k_B T.$$

The quantity $\gamma_\perp$ contains the adjustable parameter Γ, which can be determined by measurement of the halfwidth of spectral lines if the effect of an alternating electric field is taken into account.

Summarizing the results (31) and (38), the solution for scattering states of ions in ICR drift cells turns out to be:

$$\tilde{\Psi} = \tilde{\Phi} + r_\perp^{-1} \cdot f(\Theta, \langle z \rangle) \cdot \exp\left\{iK_\perp r_\perp + \frac{i}{\hbar} m(w \cdot r_m') + \frac{ie}{\hbar c}(A(r_m') \cdot r_\perp) - \frac{i}{\hbar} E^0 t\right\}$$

$$+ f_\|(\langle r_\perp \rangle) \cdot \exp\left\{iK_\| z - \frac{i}{\hbar} E^0 t\right\} \tag{41}$$

with

$$\tilde{\Phi} = \left(\frac{\alpha}{\sqrt{2\pi}}\right)^{1/2} \left(\frac{b}{2\pi}\right)^{1/2} \cdot \exp\left\{\frac{\alpha^2}{4}(z - a_z)^2 - \frac{b}{4}(\rho - a)^2\right\}$$

$$\cdot \exp\left\{\frac{i}{\hbar} mwx_m' + \frac{i}{\hbar}[w(\rho - a)] + \frac{ie}{\hbar c}[A(r_m') \cdot (\rho - a)]\right\}$$

and

$$f(\Theta, \langle z \rangle) = f(\Theta) \cdot \left(\frac{\alpha}{\sqrt{2\pi}}\right)^{1/2} \cdot \exp\left\{-\frac{\alpha^2}{4}(\langle z \rangle - a_z)^2\right\}$$

$$f_\|(\langle r_\perp \rangle) = f_\| \cdot \tilde{\varphi}_\perp(\langle r_\perp \rangle).$$

Solution (41) shows that both scattering amplitudes contain the wave packet of the other mode of motion as a parameter. This result is exclusively due to our separation ansatz for the wave function.

5. The Collision Cross Section

We rewrite solution (41) as

$$\tilde{\Psi} = \tilde{\Phi} + \tilde{\Psi}_\perp^1 \tilde{\Psi}_\|^0(\langle z \rangle) + \tilde{\Psi}_\|^1 \tilde{\Psi}_\perp^0(\langle r_\perp \rangle). \tag{42}$$

Utilizing the reality of the function $\tilde{\Phi}$ with regard to z we express the incoming particle flux density as

$$j_a = \frac{\hbar}{2mi}(\tilde{\Phi}^* \text{ grad } \tilde{\Phi} - \tilde{\Phi} \text{ grad } \tilde{\Phi}^*)$$

$$= |\tilde{\Psi}_\perp^0 \tilde{\Psi}_\|^0|^2 \left\{w^2 + \frac{\omega_c}{4} r_m'^2 - \omega_c w y_m'\right\}^{1/2} = \rho \cdot A^{1/2} \tag{43}$$

with

$$\rho = |\tilde{\Psi}_\perp^0 \tilde{\Psi}_\|^0|^2 = \frac{b}{2\pi} \frac{\alpha}{\sqrt{2\pi}} \cdot \exp\left\{-\frac{b}{2}(\rho - a)^2 - \frac{\alpha^2}{2}(z - a_z)^2\right\}.$$

Requiring the particle flux density to be numerically equal to the velocity of the relative motion [13, 14], that is $\rho = 1$, we have to use normalized wave functions

$$\Psi_\perp^0 = \left(\frac{2\pi}{b}\right)^{1/2} \exp\left\{\frac{b}{4}(\rho - a)^2\right\} \cdot \tilde{\Psi}_\perp^0$$

$$= \exp\left\{\frac{i}{\hbar} mwx_m' + \frac{i}{\hbar} m[w \cdot (\rho - a)] + \frac{ie}{\hbar c}[A(r_m') \cdot (\rho - a)]\right\} \tag{44}$$

$$\Psi_\|^0 = \left(\frac{\sqrt{2\pi}}{\alpha}\right)^{1/2} \exp\left\{\frac{\alpha}{4}(z - a_z)^2\right\} \cdot \tilde{\Psi}_\|^0 = 1.$$

We analogously normalize the outgoing wave functions. With these normalized outgoing wave functions we obtain the outgoing particle flux density

$$j_{sc} = \frac{v_\perp + (\omega_c/2)r_m'}{r_\perp^2} |f(\Theta)|^2 + v_\| |f_\||^2$$

with

$$v_\perp = \frac{\hbar K_\perp}{m} \quad \text{and} \quad v_\| = \frac{\hbar K_\|}{m}. \tag{45}$$

Using Eq. (43) with normalized wave functions we find the following connection between the differential scattering cross section and the scattering amplitudes:

$$d\sigma = \frac{j_{sc}}{j_a} r_\perp \, d\Theta \, dz$$

$$= \left\{ \frac{v_\perp + (\omega_c/2)r_m'}{r_\perp^2 A^{1/2}} |f(\Theta)|^2 + \frac{v_\|}{A^{1/2}} |f_\||^2 \right\} r_\perp \, d\Theta \, dz \tag{46}$$

with

$$|f(\Theta)|^2 = \tfrac{9}{16}\gamma_\perp^4 \delta_\perp^5 \cos^2 \Theta \quad \text{and} \quad |f_\||^2 = (2\pi)^{1/2}\gamma_\|^4 \delta_\| 2K_\| \exp(-2\delta_\|^2).$$

Integrating with regard to z and the scattering angle Θ and evaluating $\langle z \rangle = b_t$ and $\langle r_\perp^2 \rangle = R_c^2$, respectively, we obtain the total cross section

$$\sigma = \frac{v_\perp + (\omega_c/2)r_m'}{A^{1/2}} \frac{9}{16} \pi\gamma_\perp^4 \delta_\perp^5 \frac{b_t}{R_c} + \frac{v_\|}{A^{1/2}} (2\pi)^{3/2}\gamma_\|^4 \delta_\| 2K_\| \exp(-2\delta_\|^2)R_c b_t. \tag{47}$$

Applying the relations

$$(r \times p)_z = \frac{m}{2} \omega_c(r_m^2 - R_c^2) = -\hbar N \quad \text{and} \quad (N + \tfrac{1}{2})\hbar\omega_c = \frac{m}{2} \omega_c^2 R_c^2$$

(Ref. [10]) we find $R_c \gg r_m'$, and the contribution from r_m' is therefore negligible.

Replacing the abbreviations by the full terms and expressing the occurring quantities by determinable ones, we finally can write the total cross section in the form

$$\sigma = \left\{ g_1\left[\frac{1}{E_D B^2} + \frac{mc^2}{k_B T} \frac{E_D}{B^4} \right] + g_2\left[\frac{\sqrt{k_B T}}{E_D} \right] \right\} \cdot \Gamma^4$$

where

$$g_1 = \frac{36\pi c^2 \sqrt{V_t}}{\omega_t} \left(\frac{m}{e} \right)^{5/2}; \qquad g_2 = \frac{\pi^3 \exp.(-\pi/4)}{2\sqrt{e} \, \omega_t^4} \tag{48}$$

V_t = trapping potential; ω_t = trapping frequency; E_D = electric field strength which resembles in the direction $B \times w$, the Rayleigh law of scattering [15]. This expression (48) for the total cross section contains neither a quantum number nor Planck's constant h.

We have thus returned from quantum mechanics to classical theory again.

6. Conclusion

In this paper we have shown how to treat ion motion in the gas phase quantum theoretically and how to convert the result obtained to a classical one again.

Starting with the classical Langevin equation of motion for ions in ICR cells, a Schrödinger equation equivalent to the Langevin equation has been set up by the aid of the methods of Madelung and Mrowka. In order to eliminate the damping term $m\Gamma v$ we have made use of the invariance of the equation under a gauge transformation of the potentials accompanied by a phase transformation of the wave function. The Schrödinger equation found in this way contains two additional terms, namely the collision potential energy $(m/2)\Gamma^2 r^2$ and the constant imaginary quantity $(i\hbar/2)\Gamma$ which causes a constant energy displacement. We thus obtain a wave function of the type $\exp[(-\Gamma/2)t]\overline{\Psi}(r, t)$ which describes the damping process. Regarding the collision potential energy as a perturbation we have obtained the solution for the scattering states which consists of the free wave packet and outgoing waves. Normalizing the wave functions to make the particle flux density numerically equal to the relative velocity we have obtained the collision cross section which can be converted to the classical quantity. This quantity can be used to evaluate rate constants in ICR if the contribution of the alternating electric field applied to the ICR cell for ion detection is taken into account. The total cross section (48) is composed of three terms, namely a first one due to cyclotron motion, a second one due to drift motion and a third one taking into account the trapping oscillation of the ion. Equation (48) shows evidently that the dependence on the electric and magnetic fields is different for each mode of motion, and the experimental conditions therefore determine which mode of motion becomes dominant.

According to the dominant term, σ shows a different behavior. But in general σ increases with increasing Γ and therefore with increasing pressure.

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