Theoret. Chim. Acta (Berl.) 45, 137–145 (1977)

THEORETICA CHIMICA ACTA

© by Springer-Verlag 1977

Quantum-Theoretical Treatment of Motions of Ions in Ion Cyclotron Resonance Cells

Hermann Hartmann und Kyu-Myung Chung

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

A quantum-mechanical treatment of the power absorption of ICR ions based on a minimized wavepacket-approach is presented. With the aid of minimum wavepackets constructed using the exact wavefunctions for the ion motions in a homogeneous magnetic field, the power absorption of the ions in cyclotron resonance has been treated within the framework of the linear response theory. The result agrees with that obtained according to the projection-operator formalism.

Key words: Ion cyclotron resonance (ICR) – Ions in ICR cells, quantum mechanical treatment of ~

1. Introduction

Recently, Atkins and Clugston [1] have treated the power absorption of ions in ion cyclotron resonance quantum mechanically. Their work is based on the projection-operator formalism [2]. They could show that their formalism, in the linear response approximation, yields the comprehensive spectral function derived by Comisarow [3]. The comprehensive theory reduced to the Buttrill [4] and Beauchamp [5] expressions in the appropriate limits.

According to Ehrenfest's theorem, any quantum mechanical description of the power absorption theory should involve the results obtained with the classical description. The benefit of the quantum mechanical description is that one can present a theory which is not of *ad hoc* nature and which does not suffer from restrictions. In this sense, the method of Atkins and Clugston [1] is more useful than the comprehensive theory. So long as the correlation functions cannot be calculated from the wavefunctions, one has to decouple the equation of motion of Green's functions and to find the Green's function $G(E)$ and, with the aid of the latter, expressions for the correlation-functions. However, this is often very difficult, and therefore one makes use of experimental data.

To circumvent this difficulty we tackle this nearly classical problem quantum mechanically employing the minimized wavepacket approach for the ion motions in the ICR cells. We express the ensemble mean value of the ion-currents according to the linear response theory [6–7] with regard to the perturbation due to an electric field uniform in space and alternating periodically with time. Using wavepackets perturbed through the ion-molecule interaction, we approximately evaluate the time correlation function of velocity. This procedure leads to the expression for the collision rate which agrees with Atkins' and Clugston's result. This quantity, namely the collision rate, is evaluable for the specified ion-molecule interaction. An alternative expression for the collision rate is presented for the case of an unspecified ion-molecule interaction.

2. Wavepacket Approach for the ICR Ion in Homogeneous Magnetic Fields

The field existing in ICR cells is rather complicated and inhomogeneous, because the simple crossed homogeneous electric and magnetic fields are superimposed across the magnetic field direction and the pulsing electric field between the drift plates. The trapping effect on the cyclotron frequency is negligibly small, so that we can neglect the trapping potential here. Because our main concern is the power absorption at present, we also neglect the drift potential which causes the ions to move in the direction $\boldsymbol{E} \times \boldsymbol{B}$], the resulting velocity being $v = c \cdot |\boldsymbol{E}|/|\boldsymbol{B}|$, but which contributes nothing to the power absorption. The ions perform a circular motion in a plane perpendicular to the magnetic field and may collide with the neutral background gas molecules in the cell and undergo the ion-molecular interaction H_{im}. During this motion the ions absorb the power from the alternating rf electric field and induce the signal currents in the measuring plates.

The coupled ion-molecule system which is perturbed through the pulsing electric field may be separated in the translational motion of the centre of mass and the relative motion of an ion of the reduced mass μ. Disregarding the translational motion of the centre of mass we can write the Hamiltonian with the magnetic vector potential $A(\boldsymbol{r}_\perp) = \boldsymbol{B}/2 \times \boldsymbol{r}_\perp$, where $\boldsymbol{r}_\perp = \{x, y\}$, the ion-molecule interaction H_{im}, and the perturbation H_1 due to the pulsing electric field

$$H = H_0 + H_1 \tag{1}$$

where

$$H_0 = \frac{1}{2\mu}\left(P - \frac{q}{c}A\right)^2 + H_{\mathrm{im}} \tag{2}$$

Furthermore, we consider the ion-molecule interaction in the coupled ion-molecule system to be a small perturbation to the ion motion in the homogeneous magnetic field.

The motion of a charged particle in a homogeneous magnetic field has been investigated by many authors. For the symmetric gauge of the vector potential A, the exact wavefunction [8–9] is available. This wavefunction is characterized by the Landau quantum number n, the momentum in the magnetic field direction $\hbar k_z$ and the centre of the orbits r_M as parameters. If we write, for the sake of brevity, $b = qB/\hbar c$ and $\varphi = \operatorname{arctg}\,(y - y_M/x - x_M)$ we get

$$\begin{aligned} u_{n,k_z}(r, r_M) &= \frac{1}{\sqrt{L_z}}\, e^{ik_z \cdot z} \\ &\times \sqrt{\frac{b}{2\pi}\left(\frac{b}{2}\right)^n \frac{1}{n!}}\, \exp\left\{\frac{iq}{\hbar c}\,(A(\boldsymbol{r}_M), \boldsymbol{r}_\perp) - \frac{b}{4}\,(\boldsymbol{r}_\perp - \boldsymbol{r}_M)^2\right\} \\ &\times |\boldsymbol{r}_\perp - \boldsymbol{r}_M|^n\, e^{-in\varphi} \end{aligned} \tag{3}$$

This wavefunction indicates that the ion motion in the magnetic field direction is not constrained, whereas the motion in the plane perpendicular to the magnetic field it is constrained (through the magnetic field). To apply this wavefunction for the description of ion motions is not sufficiently adequate for this problem, as very high quantum numbers are involved because of $\hbar\omega_c \ll kT$. That is, the Landau energy levels are lying closely together. Therefore, the system would show a nearly classical behavior, and we may apply a wavepacket solution of this system which may be constructed with the aid of the exact wavefunctions and be minimized according to the uncertainty principle.

The construction of the wavepackets can be accomplished using the superposition principle of quantum mechanics. A general solution of the Landau problem can be expressed in the product form $\psi(r, t) = \psi_r(z, t) \cdot \psi_\perp(r, t)$, and $\psi_\perp(r, t)$ can be expanded in terms of the stationary wavefunction (3)

$$\psi_\perp(r, t) = e^{-i(\omega_c/2)t} \sum_n a_n u_n(r, r_M)\, e^{-in\omega_c t} \tag{4}$$

with the arbitrary constants a_n, which should be determined for the minimum wavepacket. Thus $\psi_\perp(r, t)$ is, apart from the phase factor $e^{-i(\omega_c/2)t}$, a periodic function of time, its period being that of the classical circular motion $2\pi/\omega_c$. This suggests that it might be possible to find a solution in the form of a wavepacket. To investigate this possibility, we calculate the uncertainty product of the radius of circular motion $\boldsymbol{R} = \boldsymbol{r}_\perp - \boldsymbol{r}_M$ and the velocity of the ions in the plane perpendicular to the magnetic field $\boldsymbol{v}_\perp = 1/\mu(P - q/cA)$. The uncertainty is defined as the root mean square deviation from the expectation value, i.e. $(\Delta R)^2 = \langle R^2 \rangle - \langle R \rangle^2$ and $(\Delta v_\perp)^2 = \langle v_\perp^2 \rangle - \langle v_\perp \rangle^2$. The uncertainty product turns out to be

$$\Delta R\, \Delta v_\perp = \sqrt{(n + \tfrac{1}{2})(n + 1)}\; 2\hbar/\mu \tag{5}$$

and has the minimum possible value of $\sqrt{2}\,\hbar/\mu$ for the ground state wavefunction

$$u_0(r, r_M) = \left(\frac{b}{2\pi}\right)^{1/2} \exp\left\{\frac{iq}{\hbar c}\,(A(\boldsymbol{r}_M), \boldsymbol{r}_\perp) - \frac{b}{4}\,(\boldsymbol{r}_\perp - \boldsymbol{r}_M)^2\right\} \tag{6}$$

This wavefunction has the form of the minimum wavepacket. Therefore, we assume that at $t = 0$ the general solution (4) has the form of the normalized minimum packet

(6), except that the radius of the classical circular motion $\boldsymbol{R}$ is changed by an amount $\boldsymbol{a}$:

$$\psi_{\perp}(r,0)=\left(\frac{b}{2\pi}\right)^{1/2}\exp\left\{\frac{iq}{\hbar c}(A(\boldsymbol{r}_M),\boldsymbol{R}-\boldsymbol{a})-\frac{b}{4}(\boldsymbol{R}-\boldsymbol{a})^2\right\}$$

$$=\sum_{n=0}a_n u_n(\boldsymbol{r}_{\perp},\boldsymbol{r}_M) \tag{7}$$

Making use of the orthogonality of the wavefunctions (3), a particular coefficient a_n can be determined and we get, if we abbreviate $\gamma=\mathrm{arctg}\,(A_y(\boldsymbol{r}_M)/A_x(\boldsymbol{r}_M))$ and $\kappa=b/2|\boldsymbol{r}_M|$

$$a_n\equiv p_n(\kappa|\boldsymbol{a}|)=\sqrt{\left(\frac{b}{2}\right)^n\frac{1}{n!}}\,\mathrm{e}^{in(\gamma+[\pi/2])}I_n(\kappa|\boldsymbol{a}|)\,\mathrm{e}^{-(b/4)a^2}|\boldsymbol{a}|^n \tag{8}$$

where the $I_n(\kappa|\boldsymbol{a}|)$ are Bessel functions. The weight function $p_n(\kappa|\Delta R|)$ turns out to be, for the deviation $\boldsymbol{a}$ from the classical radius of the circular motion comparable with the minimum uncertainty of the radius $\boldsymbol{a}\sim\Delta R=\sqrt{(n+1)2/b}\,|_{n=0}=\sqrt{2/b}$,

$$p_n(\kappa|\Delta R|)=\frac{1}{\sqrt{\mathrm{e}\,n!}}\,\mathrm{e}^{in(\gamma+[\pi/2])}I_n(\kappa\sqrt{2/b}) \tag{9}$$

Inserting this weight function (9) into (4), we obtain

$$\psi_{\perp}(r,t)=\sum_n p_n(\kappa\sqrt{2/b})u_n(\boldsymbol{r}_{\perp},\boldsymbol{r}_M)\,\mathrm{e}^{-i(n+[1/2])\omega_c t} \tag{10}$$

This is the minimized wavepacket solution for the Landau problem, and the wave function can be written putting in the characteristic quantities n, hk_z, r_M, and $\boldsymbol{a}$ as follows

$$\psi_{n,k_z}(\boldsymbol{r},\boldsymbol{r}_M,\boldsymbol{a})\equiv\langle\boldsymbol{r}|n,k_z;\boldsymbol{r}_M,\boldsymbol{a}=\sqrt{2/b}\rangle \tag{4a}$$

The maximum weight is assumed at $R=\sqrt{(n+\frac{1}{2})2/b}$ so that the classical radius of the corresponding eigenstate $|n,k_z;\boldsymbol{r}_M\rangle$ is equal to the average radius of the wavepacket. Therefore, we may conclude that the relative width

$$\frac{\Delta R}{R}=\frac{\Delta E}{E}=(n+\tfrac{1}{2})^{-1/2}=\left(\frac{\hbar\omega_c}{E}\right)^{1/2} \tag{11}$$

at energies close to the thermal energy and in magnetic fields up to 10^4G reaches at best values up to 10^{-3}, so that actually only a very narrow region ΔE contributes to the wavepacket (10). We shall use this wavepacket as the zeroth order approximation for the ion-molecule coupled system for the evaluation of power absorption in the following section.

3. Linear Response ICR Power Absorption

It is essential for the power absorption to determine the current caused by the electric field $E(t)$, which is uniform in space and alternates periodically with time, the frequency being ω_1:

$$E(t) = E_1 \hat{y} \cos \omega_1 \tau \, e^{\eta\tau}, \quad \hat{y} = \frac{y}{|y|} \tag{12}$$

because this current induces the signal voltage in the drift plates, and this signal voltage is the quantity actually measured. Inserting $d = q \cdot r$ for the dipole operator, the perturbation operator corresponding to (12) is equal to

$$H_1 = -E\, dy \cos \omega_1 \tau \, e^{\eta\tau} \tag{13}$$

Under the influence of the perturbation (13), an electric current is induced in the drift plates, which can be determined with the aid of the interaction picture for the current operators $j(t) = \exp(iH_0 t/\hbar) \cdot j(0) \exp(-iH_0 t/\hbar)$ as follows:

$$\langle j(t) \rangle = \langle j(t) \rangle_0 + \frac{1}{i\hbar} \int_{-\infty}^{t} d\tau \langle [j(t), H_1(\tau)] \rangle \tag{14}$$

where $\langle \cdots \rangle$ indicates that we have to average over a great canonical ensemble, the averaging operation being:

$$\langle \cdots \rangle = \frac{\sum_{\nu} \langle \nu | e^{-H/\theta} \cdots | \nu \rangle}{\sum_{\nu} \langle \nu | e^{-H/\theta} | \nu \rangle} \tag{15}$$

where $\theta = k_B T$ and $|\nu\rangle$ are the eigenstate vectors of the coupled ion-molecule system $H_0 = 1/2\mu(P - q/cA)^2 + H_{\mathrm{im}}$. The ensemble average of the equilibrium state $\langle j(t) \rangle_0$ disappears because there arises no net current under the influence of the magnetic field alone.

For the sake of convenience, we introduce a complex density of currents and dipole strength. The density of the n_i^+ ion currents per unit volume is related to the ionic velocity in the magnetic field according to

$$j_\pm(t) = n_i^+ q v_\pm(t) = n_i^+ q \frac{\hbar}{im} \left\{ \frac{\partial}{\partial x} \pm i \frac{\partial}{\partial y} - \frac{b}{2}(x \pm iy) \right\}(t) \tag{16}$$

The dipole strength is equal to

$$d_\pm(t) = q(x \pm iy)(t) \tag{17}$$

Dropping the vanishing ensemble average $\langle j(t) \rangle_0$, we obtain the following representation for the average currents:

$$\langle j_\pm(t) \rangle = \frac{i n_i^+ q}{\hbar} E_1 \int_{-\infty}^{t} d\tau \langle [v_\pm(t), d_\mp(\tau) \rangle \, e^{i\omega_1 \tau + \eta\tau} \tag{18}$$

Integrating by parts, we write Eq. (18) in the form

$$\langle j_\pm(t)\rangle = \frac{in_i^+ q}{\hbar} E_1 \left\{ \langle [v_\pm(0), d_\mp(0)] \rangle \frac{e^{i\omega_1 t + \eta t}}{i\omega_1 + \eta} - \int\limits_{-\infty}^{t} d\tau \langle [v_\pm(t), \dot{d}_\mp(t)] \rangle \frac{e^{i\omega_1 \tau + \eta\tau}}{i\omega_1 + \eta} \right\} \tag{19}$$

Noting that

$$\dot{d}_\mp(\tau) = qv_\mp(\tau), \qquad [v_\pm(0), d_\mp(0)] = 2\frac{\hbar \cdot q}{i\mu}$$

and using the relation

$$\sigma_\pm(\omega) = \frac{\partial}{\partial E_1} j_\pm(\omega) = \frac{\partial}{\partial E_1} \int\limits_0^\infty dt\, e^{-i\omega t} \langle j_\pm(t) \rangle$$

we get the conductivity tensor from Eq. (19):

$$\sigma_\pm(\omega) = -i\frac{n_i^+ q^2}{\mu\omega} - \frac{n_i^+ q^2}{\hbar\omega} \int\limits_0^\infty dt' \langle [v_\pm(t'), v_\mp(0)] \rangle e^{-i\omega t'} \quad (t' = t - \tau) \tag{20}$$

The first term in (20) corresponds to the electrical conductivity of the system of free ions and is not connected with the ion-molecule interaction. The calculation of the power spectrum depends on the evaluation of the correlation function $\langle [v_\pm(t'), v_\mp(0)] \rangle$. This time correlation function of the velocities may be rearranged with the aid of the definition of the ensemble averaging operation, making use of the principle of completeness of the eigenfunctions of the coupled ion-molecule system H_0 as is usually done in the dispersion relation theory [10].

Performing this step and using the relation between the symmetrized and the non-symmetrized velocity time correlation functions $\langle \{v(t)v(\tau)\}_+ \rangle = \frac{1}{2}(\exp(-\hbar\omega/\theta) + 1)\langle v(t)v(\tau) \rangle$ we can express the conductivity tensor in the quantum form of the Nyquist relation, as generalized by Callen and Welton [11] in the absence of magnetic fields

$$\sigma_\pm(\omega) = -i\frac{n_i^+ q^2}{\mu\omega} - \frac{n_i^+ q^2}{\hbar\omega} \tanh\frac{\hbar\omega}{2\theta} \int\limits_{-\infty}^{\infty} dt'\, e^{-i\omega t'} G_{\pm\mp}(t') \tag{21}$$

where the time correlation function is defined by

$$G_{\pm\mp}(t-\tau) = \langle \{v_\pm(t) v_\mp(\tau)\}_+ \rangle \tag{22}$$

Our problem is now to evaluate the time correlation function (22) which satisfies the equation of motion

$$\dot{G}_{\pm\mp}(t-\tau) = \frac{1}{i\hbar} \langle \{[v_\pm(t'), H_0], v_\mp(0)\}_+ \rangle \tag{23}$$

The Green's function method which is normally used to tackle the problems of evaluation of time correlation functions, does not necessitate any knowledge about the eigenfunctions of the system. On the other hand, one is confronted with the problems of decoupling a chain of coupled equations for the Green's functions. Moreover, one has to assume that the Fourier transform of the double time Green's function is found somehow. Proceeding that way one may construct from $G(E)$ the expressions for the time correlation functions. This decoupling procedure is sometimes very complicated. Therefore, we are going to solve the equation of motion (23) with the aid of approximate eigenfunctions.

Using the Hamiltonian $H_0 = \bar{H}_0 + H_{\text{im}}$ where $\bar{H}_0$ is the Hamiltonian for an ion in magnetic fields, we can separate the time correlation function in (23) into two parts:

$$\dot{G}_{\pm\mp}(t) = \frac{1}{i\hbar} \langle \{[v_\pm(t), \bar{H}_0], v_\mp(0)\}_+ \rangle + \frac{1}{i\hbar} \langle \{[v_\pm(t), H_{\text{im}}], v_\mp(0)\}_+ \rangle \tag{24}$$

Carrying out the ensemble average operation we make use of the first order approximation for the eigenfunction of H_0

$$|v\rangle^{(1)} = |n\rangle + \sum_{m \neq n} (E_n - \bar{H}_0 + i\hbar\zeta)^{-1} \cdot |m\rangle\langle m|H_{\text{im}}|n\rangle \tag{25}$$

and the high temperature approximation expression for the ensemble average with the eigenfunctions of the zeroth order approximation

$$\langle \{v_\pm(t), v_\mp(0)\}_+ \rangle_0 \, e^{i\omega mnt} = \frac{2}{\mu\beta} \quad \beta = \frac{1}{k_B T}, \; \omega_{mn} = \omega_m - \omega_n. \tag{26}$$

This approximation is applicable for most experimental conditions, and the restriction is not a very strict one, the maximum value for $(\hbar\omega_c/\mathrm{k}_B\mathrm{T})^{1/2}$ is 10^{-3}. Assuming that the odd powers of the transition moments $\langle n|H_{\text{im}}|m\rangle$ vanish, and making use of the fact that v_+ and v_- are the lowering and the raising operators, respectively, for the wave function $u_n(r_\perp; r_M)$ the equation of motion for the time correlation function (24) becomes

$$\dot{G}_{\pm\mp,0}(t) = (\pm; \omega_c - \xi_\pm) G_{\pm\mp,0}(t) \tag{27}$$

where ξ is the collision rate

$$\xi = \frac{\mu\beta}{2\hbar^2} \int_0^\infty dt' \langle \{[v_\pm(t') H_{\text{im}}][H_{\text{im}} v_\mp(0)]\}_+ \rangle_0 \tag{28}$$

This is the collision rate which Atkins and Clugston [1] have obtained recently using the projection operator techniques. Evaluation the ensemble average with zeroth order approximation eigenfunctions and using the relation (26), we can express the collision rate in a more familiar way, namely

$$\xi = \frac{2\pi}{\hbar} \sum_{l, m \neq n} |\langle l|H_{\text{im}}|m\rangle|^2 \, \delta(E - E_{lm}) \tag{29}$$

where the state vectors $|l\rangle$ and $|m\rangle$ correspond to the states for the wavepacket $|l\rangle \equiv |n', k_z'; r_M', \Delta R = \sqrt{2/b}\rangle$ and $|m\rangle = |n'', k_z''; r_M'', \Delta R = \sqrt{2/b}\rangle$.

The equation of motion (27) is readily solved for the initial condition $G_{\pm\mp,0}(0) = \langle\{v_\pm(0)v_\mp(0)\}_+\rangle_0 = 2/\mu\beta$. Inserting this solution into Eq. (21) and performing the high temperature approximation, we obtain for $\xi \ll \omega$ and $\delta\omega = |\omega - \omega_c| \ll \omega + \omega_c$

$$\sigma_\pm(\omega) = -i\frac{n_i^+ q^2}{\mu\omega} - \frac{n_i^+ q^2}{\mu}\left(\frac{\xi - i\,\delta\omega}{\xi^2 + \delta\omega^2}\right)(1 - \exp(-(i\,\delta\omega + \xi)t)). \tag{30}$$

The currents induced by the pulsing electric fields in the drift plates can be deduced from Eq. (30) and Ohm's law as

$$j_y \approx (n_i^+ q^2 E_1/2\mu)\,\mathrm{Re}\left\{\left(\frac{\xi - i\,\delta\omega}{\xi^2 + \delta\omega^2}\right)[1 - \exp(-(i\,\delta\omega + \xi)t]\,\mathrm{e}^{i\omega t}\right\} \tag{31}$$

It is obvious that this current induced by the electric field $E(t) = E_1 y/|y| \cos\omega_1 t$, after performing the cycle average, yield the power absorption expression which is the comprehensive spectral function by Comisarow [3], as Atkins and Clugston have shown in their paper. It is also obvious that the comprehensive spectral function leads to the functions for high and low pressures. Therefore, there is no need to give further details in this paper.

4. Discussion

In this paper, a quantum mechanical treatment of the motion of the ICR ions has been given. For the investigation of the nearly classical behavior of ions we have used the minimized wavepacket solution with which we could treat the power absorption problem quantum mechanically. Knowing about the wavepacket solution and about the wavepacket perturbed through the ion-molecule interactions, and assuming the completeness of the eigenfunctions for the coupled ion-molecule system, the expression for the collision rate is obtained. This expression is equivalent to that of Atkins and Clugston. Thus we have avoided the decoupling procedure of the chain of equations for the double time correlation functions and the analytical continuation of Green's functions $G(E)$ in the region of complex E. Furthermore, we have presented the expression for the collision rate in a more familiar form with which we may evaluate the half width of collisionally broadened ICR spectral lines and compare them with measurements, if the ion-molecule interactions are specified.

Acknowledgements. One of us (K.C.) wishes to thank the Akademie der Wissenschaften und der Literatur zu Mainz for financial help.

References

1. Atkins, P. W., Clugston, M. J.: Mol. Phys. **31**, 603 (1976)
2. Kivelson, D., Ogan, K.: Advan. Magn. Reson. **7**, 71 (1974)

3. Comisarow, M. B.: J. Chem. Phys. **55**, 205 (1971)
4. Buttrill, S. E.: J. Chem. Phys. **50**, 4125 (1969)
5. Beauchamp, J. L.: J. Chem. Phys. **46**, 1231 (1967)
6. Kubo, R.: J. Phys. Soc. Japan **12**, 570 (1957)
7. Zubarev, D. N.: Usp. Fiz. Nauk **71**, 71 (1960)
8. Jannussis, A.: Phys. Status Solidi **6**, 217 (1964)
9. Chung, K. M., Mrowka, B.: Z. Physik **259**, 157 (1973)
10. Toll, J. S.: Doctoral Diss., Princeton University (1952)
11. Callen, H. B., Welton, T. A.: Phys. Rev. **83**, 34 (1951)

Received February 3, 1977