Quantum Dispersion Theory in the Early 20s

A. Duncan and M. Janssen

1   Introduction

Heisenberg's breakthrough to matrix mechanics was directly stimulated by studies of interaction of quantized material systems with electromagnetic radiation which came to a head in the Kramers-Heisenberg paper on dispersion theory in January 1925. In this talk, we will review the important contributions of Kramers, van Vleck, and Born to this subject. Important results from classical physics will also be reviewed: the hope is that the presentation should be as far as possible comprehensible to an audience familiar with basic classical mechanics (including Hamilton's equations), electromagnetic theory (in particular, dipole radiation), and elementary quantum theory.

Lecture 1

- Review of contact transformations, action-angle variables (example: 1D SHO)

- Classical results for charged oscillators: (i) emission, (ii) absorption, (iii) polarization

- Correspondence principles (van Vleck) for emission, absorption (linear oscillator)

- Kramers dispersion formula and correspondence principle for polarization (linear oscillator)

Lecture 2

- Hamilton-Jacobi perturbation theory for linear oscillator

- Generalization of polarization results for multiply-periodic case (van Vleck,Born)

- Formal Correspondence Rule and the Classical Limit

- Modern derivation of Kramers polarization formula

Review of canonical transformations, action-angle variables

classical Hamiltonian system with phase space coordinates $(q_i, p_i), i = 1, 2, ..N$, Hamiltonian $H(p_i, q_i)$

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \tag{1}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} \tag{2}$$

a contact transformation

$$q_i' = q_i'(q_i, p_i, t) \tag{3}$$

$$p_i' = p_i'(q_i, p_i, t) \tag{4}$$

is a functional transformation of the phase space coordinates preserving the form of the Hamiltonian equations:

$$\dot{q}_i' = \frac{\partial H'}{\partial p_i'} \tag{5}$$

$$\dot{p}_i' = -\frac{\partial H'}{\partial q_i'} \tag{6}$$

Hamiltonian equations (1,2,5,6) must hold simultaneously $\Rightarrow$ variational principle

$$\delta \int \left(\sum_i p_i \dot{q}_i - H(p_i, q_i) - \sum_i p'_i \dot{q}'_i + H'(p'_i, q'_i) \right) dt = 0 \quad (7)$$

implies

$$\left\{ \sum_i p_i \dot{q}_i - H(p_i, q_i) - \sum_i p'_i \dot{q}'_i + H'(p'_i, q'_i) \right\} dt = dF \quad (8)$$

dependence of F on the $4N+1$ variables $(p_i, q_i, p'_i, q'_i, t)$ can be reduced to $2N+1$ variables via the transformation equations (3,4). Write F as $F = F(q_i, q'_i, t)$ then the partial derivatives of F can be read off directly from (8):

$$\frac{\partial F}{\partial t} = H' - H \quad (9)$$

$$\frac{\partial F}{\partial q_i} = p_i \quad (10)$$

$$\frac{\partial F}{\partial q'_i} = -p'_i \quad (11)$$

If $\frac{\partial H'}{\partial q'_i} = 0$ the new coordinates are called "angle" variables, while the new momenta p'_i are time-independent "action variables". $\dot{q}'_i = \frac{\partial H'}{\partial p'_i} = \text{constant} \equiv \nu_i$ leads to a *linear time-dependence* of the new coordinates $q'_i = \nu_i t$.

conventional notation: $p'_i \rightarrow J_i$, $q'_i \rightarrow w_i$

Example: 1 dimensional simple harmonic oscillator

Hamiltonian for 1D SHO

$$H = \frac{1}{2m}p^2 + \frac{1}{2}m\omega_0^2 q^2 \qquad (12)$$

consider following contact transformation:

$$F = \frac{1}{2}m\omega_0 q^2 \cot(q') \qquad (13)$$

which leads to the following relations between old/new coordinates:

$$p = \sqrt{2m\omega_0 p'}\cos(q') \qquad (14)$$

$$q = \sqrt{\frac{2p'}{m\omega_0}}\sin(q') \qquad (15)$$

The new Hamiltonian is simply:

$$H' = H = \omega_0 p' \qquad (16)$$

so the new coordinate variable q' is ignorable, as desired. The Hamiltonian equation for the latter implies

$$\dot{q}' = \frac{\partial H}{\partial p'} = \omega_0 \rightarrow q' = \omega_0 t + \epsilon \qquad (17)$$

Instead of the canonically conjugate variables p', q' it is usual to employ rescaled action/angle variables, defined by

$$J \equiv 2\pi p', \quad w \equiv \frac{1}{2\pi} q' \tag{18}$$

which reduce to $J = H/\nu_0$ and $w = \nu_0 t + \epsilon$ (appropriately redefining the arbitrary phase ϵ) for our 1D oscillator. The connection to the terminology "action" variable is easily seen in this simple example:

$$
\begin{align}
J &= \oint p\, dq \tag{19} \\
&= \oint m\omega_0 \sqrt{\frac{2p'}{m\omega_0}} \cos\left(q'\right) \sqrt{\frac{2p'}{m\omega_0}} \cos\left(q'\right) dq' \tag{20} \\
&= \int_0^{2\pi} 2p' \cos^2\left(q'\right) dq' \tag{21} \\
&= 2\pi p' \tag{22}
\end{align}
$$

The result (15) represents the equation of motion of the oscillator $x(t) = q(t) = D\cos\left(2\pi\nu_0 t\right) = D\cos\left(2\pi w\right)$ For the 1D SHO, the amplitude D is a function of the action variable $D = \sqrt{\frac{J}{\pi m\omega_0}}$, *but the frequency ν_0 is not!*

Classical Charged Oscillator: Emission

Classical Oscillator (in vacuo) loses energy (Larmor formula):

$$P(t) = -\frac{dE}{dt} = \frac{2}{3}\frac{e^2}{c^3}\dot{v}^2 \tag{23}$$

ascribe energy loss to a radiative reaction force given by

$$F_{\text{rad}} = \frac{2e^2}{3c^3}\ddot{v} \equiv m\tau\ddot{v} \simeq -m\tau\omega_0^2 v \tag{24}$$

For $\omega_0\tau << 1$, equation of motion of oscillator contains resistive first order term:

$$\ddot{x} + \tau\omega_0^2\dot{x} + \omega_0^2 x = 0 \tag{25}$$

Ansatz: $x(t) = De^{-\alpha t}$, with

$$\alpha \simeq \frac{1}{2}\tau\omega_0^2 \pm i\omega_0 \equiv \Gamma/2 \pm i\omega_0 \tag{26}$$

Solution: $x(t) = De^{-\Gamma t/2}\cos\left(\omega_0 t\right)$

average power loss from the Larmor formula

$$-\frac{dE}{dt} = \frac{e^2}{3c^3}D^2\omega_0^4 = \frac{16\pi^4 e^2}{3c^3}D^2\nu_0^4 \tag{27}$$

In terms of $\Gamma = \tau\omega_0^2$ (*radiative decay constant*) equation of motion (25) can be written

$$\ddot{x} + \Gamma\dot{x} + \omega_0^2 x = 0 \tag{28}$$

Classical Charged Oscillator: Absorption

Now immerse oscillator in EM field $E_x = \mathcal{E}\cos{(2\pi\nu t)}$, spectral density $\rho(\nu)$ ($< ... >$ denotes time average)

$$\frac{1}{4\pi} < \vec{E}^2 > \ = \ \frac{3}{4\pi} < E_x{}^2 >= \rho(\nu)\Delta\nu \qquad (29)$$

$$\mathcal{E}^2 \ = \ \frac{8\pi}{3}\rho(\nu)\Delta\nu \qquad (30)$$

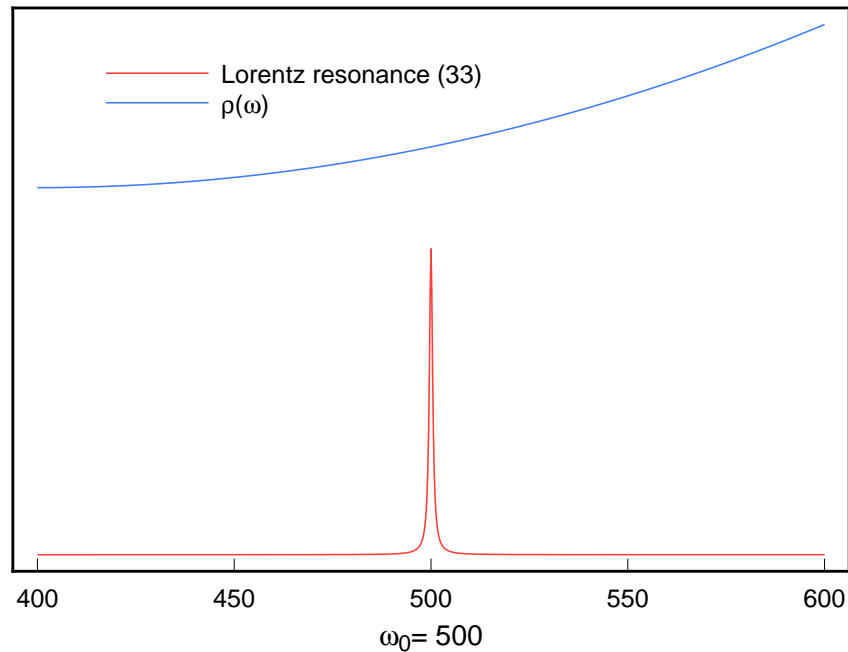Oscillator equation of motion:

$$\ddot{x} + \Gamma\dot{x} + \omega_0^2 x = \frac{e\mathcal{E}}{m}\exp{(i\omega t)} \Rightarrow x(t) = \text{Re}\ \frac{e\mathcal{E}}{m}\frac{\exp{(i\omega t)}}{\omega_0^2 - \omega^2 + i\Gamma\omega}$$
$$(31)$$

time average giving the energy absorption rate becomes

$$< F_{\text{app}}\dot{x} >=< e\mathcal{E}\cos{(\omega t)}\frac{e\mathcal{E}}{m}\text{Re}\frac{i\omega\exp{(i\omega t)}}{\omega_0^2 - \omega^2 + i\Gamma\omega} > \qquad (32)$$

Only the cosine part of the complex exponential in (32) survives in the time average; using (30), $< \cos^2{(\omega t)} >= 1/2$:

$$< F_{\text{app}}\dot{x} > \ = \ \frac{e^2\mathcal{E}^2\Gamma}{2m}\frac{\omega^2}{(\omega_0^2 - \omega^2)^2 + \Gamma^2\omega^2} \qquad (33)$$

$$= \ \frac{4\pi e^2\Gamma}{3m}\rho(\frac{\omega}{2\pi})\frac{\omega^2}{(\omega_0^2 - \omega^2)^2 + \Gamma^2\omega^2}\frac{\Delta\omega}{2\pi}$$

Legend:
Lorentz resonance (33)
$\rho(\omega)$

$\omega_0 = 500$

We've assumed $\Gamma << \omega_0$ so line resonance shape highly peaked $-- >$ use

$$\frac{\epsilon}{x^2 + \epsilon^2} \to \pi\delta(x), \quad \epsilon \to 0 \tag{34}$$

to execute integration over frequencies and compute the total energy absorption rate:

$$\begin{aligned} < F_{\text{app}}\dot{x} > &\approx \frac{2e^2}{3m} \int \rho(\frac{\omega}{2\pi})\Gamma\frac{\pi}{\Gamma\omega}\omega^2\delta(\omega^2 - \omega_0^2)d\omega \\ &= \frac{\pi e^2}{3m}\rho(\nu_0) \end{aligned} \tag{35}$$

This classical formula found (first?) in Planck's "Wärmetheorie"

Classical Charged Oscillator: Polarization

The polarization induced in an assembly of charged oscillators by an applied electric field $\mathcal{E}\cos(\omega t)$ is defined as the dipole moment per unit volume coherent with the applied field x-direction. The induced displacement for each oscillator is just given by

$$\Delta x(t) = \frac{e\mathcal{E}}{m}\mathrm{Re}\frac{e^{i\omega t}}{\omega_0^2 - \omega^2 + i\Gamma\omega}$$

so the resulting polarization is (neglecting Γ, valid if we are off resonance)

$$P = n_{\mathrm{osc}}e\frac{e\mathcal{E}}{m(\omega_0^2 - \omega^2)}\cos(\omega t) = n_{\mathrm{osc}}\frac{e^2\mathcal{E}}{4\pi^2 m}\frac{1}{\nu_0^2 - \nu^2}\cos(\omega t)$$

(36)

Physically more realistic situation, randomly oriented oscillators, $--$ > insert $\frac{1}{3}$ in the above expression.

NB! Polarization is only *first*-order in E, while absorption is *second*-order. The Hamilton-Jacobi perturbation theory for absorption (only van Vleck) is much more involved!

Quantum Radiation Theory a la Einstein (1917)

Ingredients: ensemble of quantized material systems ("atoms") with states labelled $r, s, ..$, N_r atoms in state r, ambient electromagnetic field with spectral density $\rho(\nu)$

Bohr frequency condition: $\nu_{rs} = \frac{E_r - E_s}{h}$

Einstein's analysis gives an average rate of energy emission of light of frequency ν_{rs} for an atom in state r as

$$\frac{dE_{r \to s}}{dt} = h\nu_{rs}(A_{r \to s} + B_{r \to s}\rho(\nu_{rs})) \qquad (37)$$

and the rate of energy absorption of light of frequency ν_{rs} by an atom in state s as

$$\frac{dE_{s \to r}}{dt} = h\nu_{rs}B_{s \to r}\rho(\nu_{rs}) \qquad (38)$$

Einstein's analysis of the requirements for thermodynamic equilibrium then yield the critical relations

$$B_{r \to s} = B_{s \to r} = \frac{c^3}{8\pi h\nu_{rs}^3}A_{r \to s} \qquad (39)$$

Correspondence Principle for Emission/Absorption (SHO)

In correspondence limit, the spontaneous emission rate from an oscillator in state r to state $s = r - 1$ should approach the classical result (27), where for a linear oscillator (a *very* special feature!) the mechanical oscillation frequency ν_0 is identical to the frequency of the emitted light ν_{rs}:

$$h\nu_{rs}A_{r\to s} \simeq \frac{16\pi^4 e^2}{3c^3}D_r^2\nu_{rs}^4 \tag{40}$$

$$A_{r\to s} \simeq \frac{16\pi^4 e^2}{3hc^3}D_r^2\nu_{rs}^3 \tag{41}$$

where D_r is the amplitude of the oscillator in the emitting state r. From the Einstein relation (39) this implies a corresponding result for the B-coefficients:

$$B_{r\to s} = B_{s\to r} = \frac{2\pi^3 e^2}{3h^2}D_r^2 \tag{42}$$

In the r'th quantized state of the linear oscillator, the action is $p' = r\hbar$ so the corresponding amplitude of the quantized motion becomes

$$D_r^{\text{qu}} = \sqrt{\frac{rh}{2\pi^2 m\nu_0}} \tag{43}$$

Quantum result (SHO) for the A coefficients becomes

$$A_{r \to r-1} = \frac{8\pi^2 e^2 \nu_0^2 r}{3mc^3} \qquad (44)$$

while the quantum result for the B coeffficients takes the form

$$B_{r \to r-1} = B_{r-1 \to r} = \frac{\pi e^2 r}{3hm\nu_0} \qquad (45)$$

The classical result

$$\frac{\pi e^2}{3m} \rho(\nu_0) \qquad (46)$$

gives the rate at which a classical charged oscillator gains energy when immersed in an ambient classical electromagnetic field.

van Vleck equates this to a "differential absorption rate": the rate of energy absorption of the oscillator in state r going to state $r + 1$ via (38) *minus* the "negative absorption" (in modern terminology, stimulated emission) induced by the field and causing the transition r to $r - 1$ (the B term in (37)).

From (45) we therefore have for the differential absorption rate of an oscillator in state r

$$
\begin{aligned}
\frac{dE_{\text{net}}}{dt} &= h\nu_0 (B_{r \to r+1} - B_{r \to r-1}) \rho(\nu_0) \\
&= h\nu_0 (B_{r+1 \to r} - B_{r \to r-1}) \rho(\nu_0) \\
&= h\nu_0 (r + 1 - r) \frac{\pi e^2}{3hm\nu_0} \rho(\nu_0)
\end{aligned}
$$

(Planck!)

$$
= \frac{\pi e^2}{3m} \rho(\nu_0)
$$

Warning! Special features of SHO here!!

1. allowed transitions alter quantum number by ± 1

2. ν_0 independent of amplitude, mechanical and radiation frequencies coincide

3. correspondence holds *even* at small quantum numbers

Correspondence Principle for Polarization (SHO)

The classical polarization result can be expressed in the Kramers form for the linear oscillator (as a difference between absorption and emission terms) by using the correspondence principle for emission:

$$A_{r+1\to r} - A_{r\to r-1} = \frac{8\pi^2 e^2 \nu_0^2}{3mc^3} \tag{47}$$

The classical polarization formula (36) for an oscillator in state r can then be reexpressed

$$P_r = 3\frac{n_{\text{osc}}c^3}{32\pi^4}\mathcal{E}\cos\left(2\pi\nu t\right)\{\frac{A_{r+1\to r}}{\nu_0^2(\nu_0^2 - \nu^2)} - \frac{A_{r\to r-1}}{\nu_0^2(\nu_0^2 - \nu^2)}\} \tag{48}$$

Kramer's dispersion formula for general multiply periodic systems is easily guessed:

$$P_r = 3\frac{n_{\text{osc}}c^3}{32\pi^4}\mathcal{E}\cos\left(2\pi\nu t\right)(\sum_s \frac{A_{s\to r}}{\nu_{sr}^2(\nu_{sr}^2 - \nu^2)} - \sum_t \frac{A_{r\to t}}{\nu_{rt}^2(\nu_{rt}^2 - \nu^2)}) \tag{49}$$

where the sum over s (resp. t) corresponds to states higher (resp. lower) than the state r. For SHO, these sums degenerate to a single term each (with $s = r + 1$, $t = r - 1$), and the difference frequencies $\nu_{sr}, \nu_{rt} = \nu_0$

Hamilton-Jacobi Perturbation Theory (SHO)

The Hamiltonian for the charged oscillator system is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 + e\mathcal{E}x\cos\left(\omega t\right) = H_0 + e\mathcal{E}x\cos\left(\omega t\right) \quad (50)$$

Absent a perturbing field, $\mathcal{E} = 0, H = H_0,$

$$x(t) = \sum_{\tau=\pm 1} A_\tau e^{2\pi i \tau \nu_0 t}, \quad A_\tau = A^*_{-\tau} \quad (51)$$

$$= \sum_\tau A_\tau e^{2\pi i \tau w}, \quad w \equiv \nu_0 t \quad (52)$$

$J = \frac{2\pi H_0}{\omega_0}$ and w form an action-angle pair

$$-\dot{J} = \frac{\partial H_0}{\partial w} = 0 \quad (53)$$

$$\frac{\partial H_0}{\partial J} = \frac{\omega_0}{2\pi} = \dot{w} = \nu_0 \quad (54)$$

The perturbation in (50) induces time-dependence in the action variables

$$-\dot{J} = \frac{\partial H_0}{\partial w} + e\mathcal{E}\frac{\partial x}{\partial w}\cos\left(2\pi\nu t\right) = e\mathcal{E}\frac{\partial x}{\partial w}\cos\left(2\pi\nu t\right) \quad (55)$$

so

$$\dot{J} = -\pi i e\mathcal{E}\sum_\tau \tau A_\tau(e^{2\pi i(\tau w + \nu t)} + e^{2\pi i(\tau w - \nu t)}) \quad (56)$$

NB: we only need J and w to first order in $\mathcal{E}$

$$\Delta J = \frac{e\mathcal{E}}{2} \sum_\tau \tau A_\tau \{ \frac{1 - e^{2\pi i(\tau\nu_0 t + \nu t)}}{\tau\nu_0 + \nu} + \frac{1 - e^{2\pi i(\tau\nu_0 t - \nu t)}}{\tau\nu_0 - \nu} \} \quad (57)$$

Next, we need the first order shift in the angle variable w:

$$\dot{w} = \frac{\partial H_0}{\partial J} + e\mathcal{E} \frac{\partial x}{\partial J} \cos\left(2\pi\nu t\right) \quad (58)$$

$$= \nu_0 + \frac{e\mathcal{E}}{2} \sum_\tau \frac{\partial A_\tau}{\partial J} (e^{2\pi i(\tau w + \nu t)} + e^{2\pi i(\tau w - \nu t)}) \quad (59)$$

Integrating from 0 to t, we find the shift in the angle variable

$$\Delta w = \frac{ie\mathcal{E}}{4\pi} \sum_\tau \frac{\partial A_\tau}{\partial J} \{ \frac{1 - e^{2\pi i(\tau\nu_0 t + \nu t)}}{\tau\nu_0 + \nu} + \frac{1 - e^{2\pi i(\tau\nu_0 t - \nu t)}}{\tau\nu_0 - \nu} \}$$

$$(60)$$

The first order shift in the original coordinate variable $x(t)$ arises from first order shifts in w and in J

$$\Delta x = \sum_{\tau'} (\frac{\partial A_{\tau'}}{\partial J} \Delta J + 2\pi i \tau' A_{\tau'} \Delta w) e^{2\pi i \tau' \nu_0 t} \quad (61)$$

$$= \frac{e\mathcal{E}}{2} \sum_{\tau, \tau'} (\frac{\partial A_{\tau'}}{\partial J} \tau A_\tau - \frac{\partial A_\tau}{\partial J} A_{\tau'} \tau') \frac{1 - e^{2\pi i(\tau\nu_0 - \nu)t}}{\tau\nu_0 - \nu} e^{2\pi i \tau' \nu_0 t}$$

$$+ \quad (\nu \to -\nu) \quad (62)$$

For SHO, multiplicity variables $\tau, \tau' \pm 1$: coherent terms come from the terms highlighted in red and require $\tau + \tau' = 0$:

$$\Delta x_{\text{coh}} = \frac{e\mathcal{E}}{2} \sum_\tau \{(\frac{\partial A_{-\tau}}{\partial J}\tau A_\tau + \frac{\partial A_\tau}{\partial J}A_{-\tau}\tau)\frac{e^{-2\pi i\nu t}}{\nu - \tau\nu_0} + (-\nu)\}$$

$$= \frac{e\mathcal{E}}{2} \sum_\tau \tau(\frac{\partial}{\partial J}|A_\tau|^2)(\frac{e^{-2\pi i\nu t}}{\nu - \tau\nu_0} + \frac{e^{2\pi i\nu t}}{-\nu - \tau\nu_0})$$

Only the cosine terms survive:

$$\Delta x_{\text{coh}} = 2e\mathcal{E}\cos(2\pi\nu t)\frac{\partial}{\partial J}(\frac{\nu_0}{\nu^2 - \nu_0^2}|A_\tau|^2) \qquad (63)$$

Multiply periodic version (van Vleck, Born):

$$x(t) = \sum_{\vec{\tau}} A_{\vec{\tau}}e^{2\pi i\vec{\tau}\cdot\vec{w}} = \sum_{\vec{\tau}\cdot\vec{\nu}>0} X_{\vec{\tau}}\cos(2\pi\vec{\tau}\cdot\vec{w})$$

$$\Delta x_{\text{coh}} = e\mathcal{E}\cos(2\pi\nu t)\sum_{\vec{\tau}}\vec{\tau}\cdot\vec{\nabla}_J(\frac{\vec{\tau}\cdot\vec{\nu}|A_{\vec{\tau}}|^2}{\nu^2 - (\vec{\tau}\cdot\vec{\nu})^2})$$

$$\vec{\tau}\cdot\vec{\nabla}_J \equiv \tau_1\frac{\partial}{\partial J_1} + \tau_2\frac{\partial}{\partial J_2} + \tau_3\frac{\partial}{\partial J_3}$$

$$P = N_r\frac{e^2}{2}\mathcal{E}\cos(2\pi\nu t)\sum_{\vec{\tau}\cdot\vec{\nu}>0}\vec{\tau}\cdot\vec{\nabla}_J(\frac{\vec{\tau}\cdot\vec{\nu}X_{\vec{\tau}}^2}{(\vec{\tau}\cdot\vec{\nu})^2 - \nu^2})$$

Formal Correspondence Rule: Recovering the Classical Limit

Kramers dispersion formula:

$$P_r = \frac{N_r c^3}{32\pi^4} \mathcal{E} \cos\left(2\pi\nu t\right) \left(\sum_s \frac{A_{s\to r}}{\nu_{sr}^2 (\nu_{sr}^2 - \nu^2)} - \sum_t \frac{A_{r\to t}}{\nu_{rt}^2 (\nu_{rt}^2 - \nu^2)} \right) \tag{64}$$

Sums over s (resp. t) refer to states higher (resp. lower) in energy than the fixed state r under consideration. Correspondence limit- take the state r to correspond to very high quantum numbers (n_1, n_2, n_3), states s, t associated in symmetrical pairs to central state r as follows:

$$s \quad \to \quad (n_1 + \tau_1, n_2 + \tau_2, n_3 + \tau_3) \tag{65}$$

$$t \quad \to \quad (n_1 - \tau_1, n_2 - \tau_2, n_3 - \tau_3) \tag{66}$$

Assume that $\vec{\tau} \cdot \vec{\nu} << \vec{n} \cdot \vec{\nu}$ so transitions $s \to r \to t$ correspond to *very slight changes* in the classical orbitals (and *differences approximate well to derivatives*)
Old Quantum theory quantization rule - $J_i = n_i h$ - leads to a new formal rule:

$$\delta_{\vec{\tau}} F(\vec{n}) \equiv F(\vec{n}) - F(\vec{n} - \vec{\tau}) \to h \vec{\tau} \cdot \vec{\nabla}_J F \tag{67}$$

Kramers polarization formula can be written

$$P_r = \frac{N_r c^3}{32\pi^4} \mathcal{E} \cos\left(2\pi\nu t\right) \sum_{\vec{\tau}} \delta_{\vec{\tau}}\left(\frac{A_{s\to r}}{\nu_{sr}^2\left(\nu_{sr}^2 - \nu^2\right)}\right) \qquad (68)$$

with $A_{s\to r}$ given by the correspondence principle for emission

$$A_{s\to r} = \frac{16\pi^4 e^2}{3hc^3} D_s^2 \nu_{sr}^3 \qquad (69)$$

where $D_s^2 = (X_{\vec{\tau}}^{(s)})^2 + (Y_{\vec{\tau}}^{(s)})^2 + (Z_{\vec{\tau}}^{(s)})^2$ is the full vector amplitude squared for the Fourier component of the classical path responsible for the transition $\vec{n} + \vec{\tau} \to \vec{n}$. Introducing (67,69) in (68) we obtain

$$
\begin{aligned}
P_r &= N_r \mathcal{E} \cos\left(2\pi\nu t\right) \frac{c^3}{32\pi^4} \frac{16\pi^4 e^2}{3hc^3} h \sum_{\vec{\tau}\cdot\vec{\nu}>0} \vec{\tau}\cdot\vec{\nabla}_J\left(\frac{\vec{\tau}\cdot\vec{\nu} D_s^2}{(\vec{\tau}\cdot\vec{\nu})^2 - \nu^2}\right) \\
&= N_r \frac{e^2}{2} \mathcal{E} \cos\left(2\pi\nu t\right) \sum_{\vec{\tau}\cdot\vec{\nu}>0} \vec{\tau}\cdot\vec{\nabla}_J\left(\frac{\vec{\tau}\cdot\vec{\nu}\frac{1}{3} D_s^2}{(\vec{\tau}\cdot\vec{\nu})^2 - \nu^2}\right) \qquad (70)
\end{aligned}
$$

With the replacement $\frac{1}{3}D_s^2 \to X_{\vec{\tau}}^2$ appropriate for randomly oriented atoms, (70) becomes identical to the previously obtained classical formula.

Kramers Dispersion Formula: Modern Derivation

The Kramers dispersion formula is easily derived in modern time-dependent perturbation theory, and the structure of the derivation throws light on the crucial role played by the dispersion formula in the genesis of matrix mechanics, as the amplitudes are immediately found to be just the matrix representatives of the position operator.

We consider a quantized charged system (valence electron) with states labeled by discrete indices $r, s, t, ...$, and Hamiltonian

$$H = H_0 + e\mathcal{E}x\cos(\omega t) = H_0 + V(t) \tag{71}$$

Work in the interaction picture; operators and states have time-dependence

$$O_{\text{int}}(t) \equiv e^{iH_0 t/\hbar}Oe^{-iH_0 t/\hbar} \tag{72}$$

$$\frac{\partial}{\partial t}|r,t>_{\text{int}} = -\frac{i}{\hbar}V_{\text{int}}(t)|r,t>_{\text{int}} \tag{73}$$

To first order in $\mathcal{E}$, the solution of (73) is

$$|r,t>_{\text{int}} = |r,0> -\frac{i}{\hbar}\int_0^t V_{\text{int}}(\tau)d\tau|r,0>$$

$$= |r,0> -\frac{i}{\hbar}e\mathcal{E}\int_0^t x_{\text{int}}(\tau)\cos(\omega\tau)|r,0>d\tau$$

Electron of charge $-e$ in state r, induced polarization at time t is the first order contribution (in $\mathcal{E}$) to

$_{\text{int}} < r, t | - ex_{\text{int}}(t) | r, t >_{\text{int}}$:

$$P_r = \frac{-i}{\hbar} e^2 \mathcal{E} \int_0^t < r | [x_{\text{int}}(\tau), x_{\text{int}}(t)] | r > \cos(\omega\tau) d\tau \quad (74)$$

Write $\cos(\omega\tau) = \frac{1}{2}(e^{i\omega\tau} + e^{-i\omega\tau})$ and insert a complete set of eigenstates of the unperturbed Hamiltonian H_0 $(1 = \sum_s |s><s|)$

$$P_r = \frac{-ie^2\mathcal{E}}{2\hbar} \sum_s \int_0^t (< r | e^{\frac{i}{\hbar} H_0 \tau} x e^{-\frac{i}{\hbar} H_0 (\tau - t)} | s >< s | x e^{-\frac{i}{\hbar} H_0 t} | r >$$

$$- \quad < r | e^{\frac{i}{\hbar} H_0 t} x e^{-\frac{i}{\hbar} H_0 (t - \tau)} | s >< s | x e^{-\frac{i}{\hbar} H_0 \tau} | r >) e^{i\omega\tau} d\tau$$

$$+ \quad (\omega \rightarrow -\omega)$$

$$= \quad \frac{-ie^2\mathcal{E}}{2\hbar} \sum_s \int_0^t (e^{i(E_r - E_s + \hbar\omega)\tau/\hbar} e^{i(E_s - E_r)t/\hbar} X_{rs} X_{sr}$$

$$- \quad e^{i(E_r - E_s)t/\hbar} e^{i(E_s - E_r + \hbar\omega)\tau/\hbar} X_{rs} X_{sr}) d\tau + (\omega \rightarrow -\omega)$$

where the matrix elements of the coordinate operator have now made their appearance: $X_{rs} \equiv < r | x | s >$

Perform the time integral, keeping only the coherent terms

$$
\begin{aligned}
P_r &= \frac{-e^2 \mathcal{E}}{2} \Big(\sum_s \frac{X_{rs} X_{sr}}{E_r - E_s + \hbar\omega} - \sum_s \frac{X_{rs} X_{sr}}{E_s - E_r + \hbar\omega} \Big) e^{i\omega t} \\
&+ \quad (\omega \to -\omega)
\end{aligned} \tag{75}
$$

The terms in (75) proportional to $\sin(\omega t)$ cancel and we are left with the real result (defining $E_r - E_s \equiv \hbar\omega_{rs}$)

$$
\begin{aligned}
P_r &= \frac{-e^2 \mathcal{E}}{\hbar} \sum_s \Big(\frac{\omega_{rs} X_{rs} X_{sr}}{\omega_{rs}^2 - \omega^2} - \frac{\omega_{sr} X_{rs} X_{sr}}{\omega_{sr}^2 - \omega^2} \Big) \cos(\omega t) \\
&= \frac{-2e^2 \mathcal{E}}{\hbar} \sum_s \frac{\omega_{rs} X_{rs} X_{sr}}{\omega_{rs}^2 - \omega^2} \cos(\omega t)
\end{aligned} \tag{76}
$$

Parity symmetry implies $X_{rs} = 0$ if $s = r$, and the sum in (76) can naturally be separated into states s of higher energy than r, with $\omega_{sr} > 0$, and states t of lower energy, with $\omega_{rt} > 0$:

$$
P_r = \frac{2e^2 \mathcal{E}}{\hbar} \Big(\sum_s \frac{\omega_{sr} X_{sr} X_{rs}}{\omega_{sr}^2 - \omega^2} - \sum_t \frac{\omega_{rt} X_{rt} X_{tr}}{\omega_{rt}^2 - \omega^2} \Big) \cos(\omega t) \tag{77}
$$

This result is valid for any H_0 with a discrete spectrum!

Use Correspondence principle for emission

$$A_{s \to r} = \frac{16\pi^4 e^2}{3hc^3} D_s^2 \nu_{sr}^3 \qquad (78)$$

and identify $D_s^2 \equiv (X_\tau^s)^2 + (Y_\tau^s)^2 + (Z_\tau^s)^2$ with $3(X_\tau^s)^2 = 12A_\tau A_{-\tau}$ and the Fourier coefficients $A_\tau \to X_{sr}$, $A_{-\tau} \to X_{rs}$

$$A_{s \to r} = \frac{64\pi^4 e^2}{hc^3} \nu_{sr}^3 X_{sr} X_{rs} \qquad (79)$$

whence follows the original form (64) of the dispersion formula

$$P_r = \frac{c^3}{32\pi^4} \mathcal{E} \cos(\omega t)(\sum_s \frac{A_{s \to r}}{\nu_{sr}^2(\nu_{sr}^2 - \nu^2)} - \sum_t \frac{A_{r \to t}}{\nu_{rt}^2(\nu_{rt}^2 - \nu^2)}) \qquad (80)$$

Of course, the above identification of classical Fourier components with matrix elements of the position operator is at the core of Heisenberg's 1925 breakthrough.

Summary

- The conceptual shift from classical to quantum theory entails a fundamental alteration of the notion of space of states: from classical phase space to Hilbert space

- Coupling of an external electromagnetic field to a quantized material system in a given stationary state provides a probe of the structure of state space, by inducing an admixture with all other accessible states:

$$|r, t >= |r > e^{-iE_r t/\hbar} \rightarrow \sum_s c_s |s > e^{-iE_s t/\hbar}$$

whence the electron displacement ($\rightarrow$polarization) acquires a dependence on *difference* frequencies:

$$< r, t|X|r, t > \rightarrow \sum_{s,s'} c_{s'}^* c_s X_{s's} e^{i(E_{s'} - E_s)t/\hbar}$$

- The "doubled" character of dynamical variables in quantum theory- initially so puzzling from a classical viewpoint- but leading finally to the matrix mechanical formulation, can be summarized in the following motto:
CLASSICAL PHASE SPACE $< --->$ SQUARE OF QUANTUM STATE SPACE