

On the verge of *Umdeutung* in Minnesota: Van Vleck and the correspondence principle. Part Two ^{*}

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Abstract

This is the second installment of a two-part paper on developments in quantum dispersion theory leading up to Heisenberg's *Umdeutung* paper. In telling this story, we have taken a paper by John H. Van Vleck (1924b,c) as our main guide. In this second part we present the detailed derivations on which our narrative in the first part rests. The central result that we derive is the Kramers dispersion formula, which played a key role in the thinking that led to Heisenberg's *Umdeutung* paper. We derive classical formulae for the dispersion, emission, and absorption of radiation and use Bohr's correspondence principle to construct their quantum counterparts both for the special case of a charged harmonic oscillator (sec. 5) and for arbitrary non-degenerate multiply-periodic systems (sec. 6). We then rederive these results in modern quantum mechanics (sec. 7).

Key words: Kramers dispersion formula, Correspondence Principle, Canonical perturbation theory, Matrix mechanics

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5 Van Vleck and the application of the correspondence principle to the interaction of matter and radiation

In the two-part paper that forms the focal point of our study, Van Vleck (1924b,c) explored in a systematic and physically cogent fashion the implications of the correspondence principle for several aspects of the interaction of matter and radiation. The paper is signed June 19, 1924 and appeared in the October 1924 issue of *The Physical Review*. In this paper, Van Vleck gives a detailed derivation of the correspondence principle for absorption, which he had introduced in a short note in the *Journal of the Optical Society in America*, signed April 7, 1924 (Van Vleck, 1924a). In addition, he thoroughly examined the issues involved in connecting Einstein's A and B coefficients to features of classical electron orbits. Finally, as we mentioned in sec. 3.4 in Part One of our paper, he showed that, in the limit of high quantum numbers, Kramers' quantum formula for polarization merges with the classical formula for polarization in arbitrary non-degenerate multiply-periodic systems.

In part I of his paper, reproduced in (Van der Waerden, 1968), Van Vleck (1924b) discusses the transition from quantum-theoretical expressions for emission, absorption, and dispersion to corresponding classical expressions that one expects to hold in the limit of high quantum numbers. It is only in part II, not included in (Van der Waerden, 1968), that Van Vleck (1924c) derives the classical expressions for absorption and dispersion of radiation by a general non-degenerate multiply-periodic system, using standard methods of canonical perturbation theory in action-angle variables. Van Vleck could assume his audience to be thoroughly familiar with these techniques. This is no longer true today. For the sake of clarity of exposition, we therefore invert the order of Van Vleck's own presentation.

In sec. 5.1, we present the basic elements of the canonical formalism in action-angle variables and use it to rederive the classical formula (6) in sec. 3.1 for the dipole moment of a charged one-dimensional simple harmonic oscillator. Though much more complicated than the derivation in sec. 3.1, this new derivation has two distinct advantages. First, it suggests a way of translating the classical formula into a quantum formula with the help of Bohr's correspondence principle and Einstein's A and B coefficients. Secondly, both the derivation of the classical formula and its translation into a quantum formula can easily be generalized to arbitrary non-degenerate multiply-periodic systems.

In sec. 5.2, we translate the classical formula for the dipole moment of a simple harmonic oscillator into a quantum formula. In sec. 5.3, we similarly convert classical formulae for emission and absorption by a simple harmonic oscillator to the corresponding quantum formulae. Both the mathematical

manipulations and the physical interpretation are particularly transparent in the case of a simple harmonic oscillator, and Van Vleck himself frequently used this example for illustrative purposes. The generalization of the various results to arbitrary non-degenerate multiply-periodic systems, which is a primary focus of Van Vleck’s paper, will be deferred to sec. 6. In sec. 7, we present (or outline) modern derivations of various results in secs. 5 and 6. In sec. 8, we summarize our conclusions.

5.1 *Deriving the classical formula for the dipole moment of a simple harmonic oscillator using canonical perturbation theory*

In this subsection we rederive formula (6) in sec. 3.4 for the dipole moment of a charged one-dimensional simple harmonic oscillator, using canonical perturbation theory in action-angle variables. Like Kramers, Van Vleck was a master of these techniques in classical mechanics. As Van Vleck recalled fifty years after the fact:

In 1924 I was an assistant professor at the University of Minnesota. On an American trip, Ehrenfest gave a lecture there . . . [He] said he would like to hear a colloquium by a member of the staff. I was selected to give a talk on my “Correspondence Principle for Absorption” . . . I remember Ehrenfest being surprised at my being so young a man. The lengthy formulas for perturbed orbits in my publication on the three-body problem of the helium atom [Van Vleck, 1922] had given him the image of a venerable astronomer making calculations in celestial mechanics (Van Vleck, 1974, p. 9).¹⁷⁶

We begin by reviewing some of the mathematical tools we need.¹⁷⁷ Consider a classical Hamiltonian system with phase space coordinates (q_i, p_i) , $i = (1, 2, \dots, N)$ and Hamiltonian $H(q_i, p_i)$, which does not explicitly depend on time. Hamilton’s equations are

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}. \quad (15)$$

¹⁷⁶Van Vleck failed to conform to Ehrenfest’s image of a young physicist in another respect. In an interview in 1973, “Van Vleck recalled, “I shocked Ehrenfest . . . when I told him I liked popular music.” Ehrenfest, he said, “thought that was completely irreconcilable with my having written any respectable papers.”” (Fellows, 1985, p. 54)

¹⁷⁷This material is covered in standard graduate textbooks on classical mechanics, such as (Goldstein, 1980), heavily influenced by (Born, 1925) (Goldstein, 1980, pp. 429, 493, 540). We recommend (Matzner and Shepley, 1991).

Consider a contact transformation $(q_i, p_i) \rightarrow (q'_i, p'_i)$ preserving the form of Hamilton's equations, in the sense that there exists a new Hamiltonian H' such that

$$\dot{q}'_i = \frac{\partial H'}{\partial p'_i}, \quad \dot{p}'_i = -\frac{\partial H'}{\partial q'_i}. \quad (16)$$

Since Hamilton's equations (15) and (16) must hold simultaneously, the variational principles

$$\delta \int_{t_1}^{t_2} \left(\sum_i p_i \dot{q}_i - H(q_i, p_i) \right) dt = 0, \quad \delta \int_{t_1}^{t_2} \left(\sum_i p'_i \dot{q}'_i - H'(p'_i, q'_i) \right) dt = 0 \quad (17)$$

for arbitrary times t_1 and t_2 must also hold simultaneously. This implies that the difference between the two integrands in eq. (17) must be a total time derivative

$$\left(\sum_i p_i \dot{q}_i - H(q_i, p_i) - \sum_i p'_i \dot{q}'_i + H'(p'_i, q'_i) \right) dt = dF, \quad (18)$$

which will not contribute to the variation of the action. The apparent dependence of F on the $4N + 1$ variables $(q_i, p_i, q'_i, p'_i, t)$ can be reduced to $2N + 1$ variables via the equations for the contact transformation $(q_i, p_i) \rightarrow (q'_i, p'_i)$. If we choose to write F as a function of the initial and final coordinates, $F = F(q_i, q'_i, t)$, then the partial derivatives of F can be read off directly from eq. (18):

$$\frac{\partial F}{\partial t} = H' - H, \quad \frac{\partial F}{\partial q_i} = p_i, \quad \frac{\partial F}{\partial q'_i} = -p'_i. \quad (19)$$

By solving (at least in principle!) the second of these three equations for q'_i as a function of (q_i, p_i) , and then substituting the result in the third to obtain p'_i , we see that the function F encodes the full information of the transformation $(q_i, p_i) \rightarrow (q'_i, p'_i)$. This function is called the *generating function* of the transformation. Given F the form of the new Hamiltonian H' can be obtained (again, in principle!) from the first of eqs. (19).

A special case of great interest occurs when the generating function F can be chosen so that the resulting Hamiltonian is independent of the new coordinates q'_i (which are then called *ignorable*). Hamilton's equations then immediately imply that the associated momenta p'_i are time-independent, and that the new coordinates q'_i are linear in time. In this circumstance the new momenta are

usually called *action variables*—the notation J_i is conventional for these—while the new coordinates are dubbed *angle variables*, with the conventional notation w_i .

To illustrate the above with a concrete example, which we shall be using throughout this section, consider a one-dimensional simple harmonic oscillator with Hamiltonian:¹⁷⁸

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2q^2. \quad (20)$$

Consider the transformation induced by

$$F = \frac{1}{2}m\omega_0q^2 \cot q'. \quad (21)$$

This function does not explicitly depend on time, so $H' = H$ (see eq. (19)). Eq. (19) also tells us that

$$p = \frac{\partial F}{\partial q} = m\omega_0q \cot q', \quad p' = -\frac{\partial F}{\partial q'} = \frac{1}{2}m\omega_0q^2 \csc^2 q'. \quad (22)$$

From the latter equation it follows that $q^2 = (2p'/m\omega_0) \sin^2 q'$ or that

$$q = \sqrt{\frac{2p'}{m\omega_0}} \sin q'. \quad (23)$$

Inserting this expression for q into the expression for p , we find

$$p = \sqrt{2m\omega_0p'} \cos q'. \quad (24)$$

Substituting eqs. (23)–(24) for q and p into eq. (20) we find

$$H = \omega_0 p'. \quad (25)$$

¹⁷⁸A short digression on the (almost inevitable) notational confusions lurking in this subject is in order. We shall continue to use the conventional notation ω to denote angular frequencies, with the ordinary frequency (reciprocal period) denoted by the Greek letter ν . Unfortunately, Van Vleck uses ω to denote ordinary frequency! Moreover, there is the embarrassing similarity of the angle variables w_i to the frequencies ω_i . Also, there is the need to distinguish between the frequencies of the isolated mechanical system ($\omega_0 = 2\pi\nu_0$ for the simple harmonic oscillator) and the frequency of an applied electromagnetic wave, which we shall denote as $\omega = 2\pi\nu$ throughout.

Since $H' = H$, this means that the new coordinate variable q' is *ignorable*, as desired. Hamilton's equations for (q', p') are:

$$\dot{q}' = \frac{\partial H}{\partial p'} = \omega_0, \quad \dot{p}' = -\frac{\partial H}{\partial q'} = 0, \quad (26)$$

from which it follows that $q' = \omega_0 t + \epsilon$ and that $p' = H/\omega_0$ is time-independent. Instead of the canonically conjugate variables (p', q') it is customary to employ rescaled action-angle variables

$$J \equiv 2\pi p', \quad w \equiv \frac{1}{2\pi} q'. \quad (27)$$

Hamilton's equations for (J, w) are:

$$\dot{w} = \frac{\partial H}{\partial J} = \nu_0, \quad \dot{J} = -\frac{\partial H}{\partial w} = 0. \quad (28)$$

It follows that $J = H/\nu_0$ and $w = \nu_0 t + \epsilon$ (appropriately redefining the arbitrary phase ϵ) for our one-dimensional oscillator.

The connection to the terminology *action variable* is easily seen in this example. In this simple case, the action is defined as the area enclosed by a single orbit of the periodic system in the two-dimensional phase space spanned by the coordinates (p, q) :

$$J = \oint p dq. \quad (29)$$

Inserting eqs. (23) and (24) into the integrand, we find

$$\oint \left(\sqrt{2m\omega_0 p'} \cos q' \right) d \left(\sqrt{\frac{2p'}{m\omega_0}} \sin q' \right) = \int_0^{2\pi} 2p' \cos^2 q' dq' = 2\pi p', \quad (30)$$

which is just the expression for J in eq. (27).

The result (23) represents, of course, the solution of the equation of motion of the oscillator

$$q(t) = D \cos 2\pi\nu_0 t = D \cos 2\pi w, \quad (31)$$

where we have chosen the phase shift ϵ to start the oscillator at maximum displacement at $t = 0$, and where the amplitude is a function of the action

variable

$$D = \sqrt{\frac{J}{m\pi\omega_0}}. \quad (32)$$

We now turn to our basic model for dispersion, i.e., a charged one-dimensional simple harmonic oscillator subjected to the periodically varying electric field of an electromagnetic wave. Earlier, we used elementary techniques of classical mechanics to analyze this system (see eqs. (2)–(6) in sec. 3.1). Although such methods are physically transparent, they depend on an explicit treatment of the equations of motion of a specific and completely specified Hamiltonian. The same results can be obtained by the methods of canonical perturbation theory, where general formulas can be obtained for the perturbation in the coordinate(s) of the system *completely independently of the specific nature of the dynamics*. As Van Vleck put it:

If we were to study the perturbations in the motion produced by the incident wave purely with the aid of [Newton’s second law] it would be impossible to make further progress without specializing the form of the potential function [such as, e.g., $\frac{1}{2}m\omega_0^2q^2$ in eq. (20)] . . . However, it is quite a different story when we seek to compute the perturbations . . . in the “angle variables” w_1, w_2, w_3 and their conjugate momenta J_1, J_2, J_3 . . . In fact by using them rather than x, y, z , which is the essential feature of the present calculation, the periodic properties of the system come to light even without knowing the form of [the potential] (Van Vleck, 1924c, p. 350).

Using canonical perturbation theory in action-angle variables, we rederive eq. (6) of sec. 3.1 for the polarization of a one-dimensional charged simple harmonic oscillator. In sec. 6.2, we turn to the general case of an arbitrary non-degenerate multiply-periodic system.

The Hamiltonian is now the sum of the Hamiltonian H_0 given by eq. (20) and a perturbative term H_{int} describing the interaction between the harmonic oscillator and the electromagnetic wave:¹⁷⁹

$$H = H_0 + H_{\text{int}} = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2x^2 + eEx \cos \omega t. \quad (33)$$

The subscript ‘0’ in ν_0 or ω_0 refers to the characteristic frequency of the unperturbed oscillator. Without subscript ν and ω refer to the frequency of the external electric field.

¹⁷⁹As before, we assume that the electric field is in the direction of motion of the oscillator (cf. sec. 3.1). It follows from eq. (33) that the force $F = -\partial V/\partial x$ of the electric field on the charge is $-eE \cos \omega t$, in accordance with eq. (3) in sec. 3.1 (recall that we use e to denote the absolute value of the electron charge).

Absent a perturbing field ($E = 0, H = H_0$), we can write $x(t)$ in terms of the action-angle variables J and $w = \nu_0 t$:

$$x(t) = \sum_{\tau=\pm 1} A_\tau(J) e^{2\pi i \tau w}, \quad (34)$$

where A_τ has to satisfy the conjugacy relation $A_\tau = A_{-\tau}^*$ to ensure that $x(t)$ in eq. (34) is real ($x(t) = x^*(t)$). Note that we have changed notation somewhat compared to eq. (31). We returned to Cartesian coordinate notation (x instead of q), and the amplitude has been redefined:¹⁸⁰

$$D = 2|A_\tau|. \quad (35)$$

The action-angle variables $J = H_0/\nu_0$ and $w = \nu_0 t$ satisfy Hamilton's equations (see eq. (28)):

$$0 = -\dot{J} = \frac{\partial H_0}{\partial w}, \quad \frac{\partial H_0}{\partial J} = \dot{w} = \nu_0. \quad (36)$$

It is a special feature of the simple harmonic oscillator that the frequency ν_0 is independent of the amplitude of motion (and thereby of the action). The generating function for the contact transformation from (x, p) to (w, J) is time-independent (cf. eq. (21)), so eq. (19) implies that the old and new Hamiltonians coincide in value (i.e., one simply reexpresses the original Hamiltonian in the new variables). Even with the perturbation turned on *we shall continue to use the same contact transformation*, computing the perturbations $(\Delta w, \Delta J)$ induced by the applied field in the action-angle variables (w, J) as an expansion in E . These are *not* action-angle variables for the full Hamiltonian $H_0 + H_{\text{int}}$, only for the unperturbed Hamiltonian H_0 (cf. Van Vleck 1926, pp. 200–201).

Eventually, we are interested in the displacement Δx in the particle coordinate (to first order in E) induced by the applied field. To first order, Δx is given by

$$\Delta x = \frac{\partial x}{\partial J} \Delta J + \frac{\partial x}{\partial w} \Delta w. \quad (37)$$

Using eq. (34) to evaluate $\partial x/\partial J$ and $\partial x/\partial w$, we can rewrite this as:

¹⁸⁰Inserting $A_\tau = |A_\tau| e^{i\varphi}$ into eq. (34), we find $x(t) = (|A_\tau| + |A_{-\tau}|) \cos(2\pi w + \varphi)$. Since $A_\tau = A_{-\tau}^*$, $|A_\tau|^2 = A_\tau A_\tau^*$ is equal to $|A_{-\tau}|^2 = A_{-\tau} A_{-\tau}^*$. The phase angle φ is immaterial.

$$\Delta x = \sum_{\tau=\pm 1} \left(\frac{\partial A_\tau}{\partial J} \Delta J + 2\pi i \tau A_\tau \Delta w \right) e^{2\pi i \tau w}. \quad (38)$$

Assuming the external field to be switched on at time zero, the first-order shifts Δw and ΔJ are given by:

$$\Delta J = \int_0^t \Delta \dot{J} dt, \quad \Delta w = \int_0^t \Delta \dot{w} dt, \quad (39)$$

where the integrands $\Delta \dot{J}$ and $\Delta \dot{w}$ are determined by Hamilton's equations.

The perturbation in eq. (33) will induce a time-dependence in the action variable, as Hamilton's equation for the action variable in the presence of the perturbing field now reads

$$\dot{J} = -\frac{\partial H_0}{\partial w} - eE \frac{\partial x}{\partial w} \cos 2\pi \nu t = -eE \frac{\partial x}{\partial w} \cos 2\pi \nu t. \quad (40)$$

Note that we still have $\partial H_0 / \partial w = 0$, so $\Delta \dot{J} = \dot{J}$. At this point it is convenient to replace $\cos 2\pi \nu t$ by $\frac{1}{2}(e^{2\pi i \nu t} + e^{-2\pi i \nu t})$. Inserting eq. (34) into eq. (40), we find

$$\Delta \dot{J} = -\pi i e E \sum_{\tau=\pm 1} \tau A_\tau \left(e^{2\pi i(\tau w + \nu t)} + e^{2\pi i(\tau w - \nu t)} \right). \quad (41)$$

To obtain the polarization, which is a linear effect in the applied field E , we only need ΔJ and Δw to first order in E . This means that the angle variables w in the exponents in eq. (41) can be taken to zeroth order, i.e., $w = \nu_0 t$. Integrating $\Delta \dot{J}$ we find:

$$\Delta J = \int_0^t \Delta \dot{J} dt = \frac{eE}{2} \sum_{\tau=\pm 1} \tau A_\tau \left\{ \frac{1 - e^{2\pi i(\tau \nu_0 t + \nu t)}}{\tau \nu_0 + \nu} + \frac{1 - e^{2\pi i(\tau \nu_0 t - \nu t)}}{\tau \nu_0 - \nu} \right\}. \quad (42)$$

Next, we need to compute the first order shift Δw in the angle variable w . Hamilton's equation for the angle variable w in the presence of the perturbation is:¹⁸¹

¹⁸¹ It is a special feature of the simple harmonic oscillator that the characteristic frequency ν_0 is independent of the amplitude and thus of the action variable J (see eq. (32)). In general, ν_0 will be a function of J . The first term on the right-hand side of eq. (43) would then become $\partial H_0 / \partial J = \nu_0(J) = \nu_0 + (\partial \nu_0 / \partial J) \Delta J$.

$$\begin{aligned}
\dot{w} &= \frac{\partial H_0}{\partial J} + eE \frac{\partial x}{\partial J} \cos 2\pi\nu t \\
&= \nu_0 + \frac{eE}{2} \sum_{\tau=\pm 1} \frac{\partial A_\tau}{\partial J} \left(e^{2\pi i(\tau w + \nu t)} + e^{2\pi i(\tau w - \nu t)} \right). \tag{43}
\end{aligned}$$

Once again, w may be replaced by $\nu_0 t$ in the exponentials in eq. (43). Integrating the second term in eq. (43), which gives the shift $\Delta\dot{w}$ due to H_{int} , we find:

$$\Delta w = \int_0^t \Delta\dot{w} dt = \frac{ieE}{4\pi} \sum_{\tau=\pm 1} \frac{\partial A_\tau}{\partial J} \left\{ \frac{1 - e^{2\pi i(\tau\nu_0 t + \nu t)}}{\tau\nu_0 + \nu} + \frac{1 - e^{2\pi i(\tau\nu_0 t - \nu t)}}{\tau\nu_0 - \nu} \right\}. \tag{44}$$

Substituting expressions (42) and (44) for ΔJ and Δw into eq. (38), we find

$$\begin{aligned}
\Delta x &= \frac{eE}{2} \sum_{\tau'=\pm 1} \sum_{\tau=\pm 1} \left\{ \frac{\partial A_{\tau'}}{\partial J} \tau A_\tau - \tau' A_{\tau'} \frac{\partial A_\tau}{\partial J} \right\} \frac{1 - e^{2\pi i(\tau\nu_0 t - \nu t)}}{\tau\nu_0 - \nu} e^{2\pi i\tau'\nu_0 t} \tag{45} \\
&\quad + (\nu \rightarrow -\nu),
\end{aligned}$$

where “ $(\nu \rightarrow -\nu)$ ” here and below is shorthand for: “the same term with ν replaced by $-\nu$ everywhere.” The coherent contribution to the polarization comes from the terms in eq. (45) with the same time-dependence as the applied field, i.e., from terms in which the time-dependence is given by the factor $e^{\pm 2\pi i\nu t}$. In the terminology of Van Vleck (1924c): “the part of the displacement which is resonant to the impressed wave” (p. 361). These are the terms in which the summation indices, which in the case of the simple harmonic oscillator only take on the values ± 1 , have opposite values, i.e., $\tau = -\tau'$. The contribution of such terms to the first-order displacement is

$$\begin{aligned}
\Delta x_{\text{coh}} &= \frac{eE}{2} \sum_{\tau=\pm 1} \left\{ \left(\frac{\partial A_{-\tau}}{\partial J} \tau A_\tau + \tau A_{-\tau} \frac{\partial A_\tau}{\partial J} \right) \frac{-e^{-2\pi i\nu t}}{\tau\nu_0 - \nu} + (\nu \rightarrow -\nu) \right\} \\
&= \frac{eE}{2} \sum_{\tau=\pm 1} \tau \frac{\partial |A_\tau|^2}{\partial J} \left\{ \frac{e^{-2\pi i\nu t}}{\nu - \tau\nu_0} - \frac{e^{2\pi i\nu t}}{\nu + \tau\nu_0} \right\}. \tag{46}
\end{aligned}$$

The imaginary part of this expression is a sum over the product of odd and even functions of the index τ ,

$$-\frac{eE}{2} \sum_{\tau=\pm 1} \tau \frac{\partial |A_\tau|^2}{\partial J} \left(\frac{1}{\nu - \tau\nu_0} + \frac{1}{\nu + \tau\nu_0} \right) \sin 2\pi\nu t, \tag{47}$$

and therefore vanishes, leaving only the real part:

$$\begin{aligned}\Delta x_{\text{coh}} &= \frac{eE}{2} \sum_{\tau} \tau \frac{\partial |A_{\tau}|^2}{\partial J} \left(\frac{1}{\nu - \tau\nu_0} - \frac{1}{\nu + \tau\nu_0} \right) \cos 2\pi\nu t \\ &= \frac{eE}{2} \sum_{\tau} \tau \frac{\partial |A_{\tau}|^2}{\partial J} \left(\frac{2\tau\nu_0}{\nu^2 - \tau^2\nu_0^2} \right) \cos 2\pi\nu t.\end{aligned}\quad (48)$$

Since $|A_{\tau}|^2 = |A_{-\tau}|^2$ (see note 180) and since τ only takes on the values ± 1 in the case of the simple harmonic oscillator, $\tau^2 = 1$ and the two terms in the summation over τ are identical. Although in this special case the derivative with respect to J only acts on $|A_{\tau}|^2$, we are free to include the expression $2\nu_0/(\nu^2 - \nu_0^2)$ within the scope of the derivative (recall that ν_0 does not depend on J in this case). Eq. (48) then becomes

$$\Delta x_{\text{coh}} = 2eE \frac{\partial}{\partial J} \left(\frac{\nu_0}{\nu^2 - \nu_0^2} |A_{\tau}|^2 \right) \cos 2\pi\nu t. \quad (49)$$

The resulting expression for the dipole moment, $p(t) = -e\Delta x_{\text{coh}}$, of a one-dimensional charged simple harmonic oscillator is a special case of the expressions for the dipole moment of a general non-degenerate multiply-periodic system with the same charge given by Kramers and Van Vleck. Kramers (1924b, p. 310, eq. 2*) denotes this quantity by P and gives the following formula:

$$P = \frac{E}{2} \sum \frac{\partial}{\partial I} \left(\frac{C^2\omega}{\omega^2 - \nu^2} \right) \cos 2\pi\nu t. \quad (50)$$

In the special case of a one-dimensional charged simple harmonic oscillator, ω , I , and C correspond to ν_0 , J , and $2|A_{\tau}|$ in our notation, respectively. There appears to be a factor e^2 missing in Kramers' formula. We shall derive the corresponding formula (41) in (Van Vleck, 1924c, p. 361) in sec. 6.2.

Eq. (49) is equivalent to eq. (6), the result of our much simpler derivation in sec. 3.1. Recalling that (cf. eqs. (31)–(32), eqs. (34)–(35) and note 180)

$$x(t) = 2|A_{\tau}| \cos 2\pi\nu_0 t = \sqrt{\frac{J}{2\pi^2 m\nu_0}} \cos 2\pi\nu_0 t, \quad (51)$$

we have $|A_{\tau}|^2 = J/(8\pi^2 m\nu_0)$, and eq. (49) reduces to

$$\Delta x_{\text{coh}} = \frac{eE \cos 2\pi\nu t}{4\pi^2 m(\nu^2 - \nu_0^2)}. \quad (52)$$

The dipole moment is thus given by:

$$p(t) = -e\Delta x_{\text{coh}} = \frac{e^2 E}{4\pi^2 m(\nu_0^2 - \nu^2)} \cos 2\pi\nu t, \quad (53)$$

in agreement with eq. (6) in sec. 3.1.

The preceding discussion employs a version of canonical perturbation theory in which a single set of action-angle variables, chosen for the unperturbed Hamiltonian, is used throughout the calculation, even after the time-dependent perturbation is switched on. Accordingly, the new action variables are no longer constant, and the new angle variables are no longer linear in time. The same classical polarization result is derived in a somewhat different manner by Born (1924) and by Kramers and Heisenberg (1925). Born performs a contact transformation in which the generating function F (cf. eq. (18)) is chosen as a function of (q_i, p'_i) , the old coordinates and the new momenta, which is then evaluated systematically order by order in the perturbation to maintain the constancy of the new action variables. In (Kramers and Heisenberg, 1925) the same procedure is followed, but as only the first order result is needed, it suffices to use the infinitesimal form of the contact transformation.¹⁸²

5.2 *Converting the classical formula for dispersion to a quantum formula in the special case of a simple harmonic oscillator*

Using Bohr's correspondence principle as our guide, we now 'translate' the classical formula (49) for displacement (and thence for polarization) into a quantum formula. Two main ingredients go into this particular application of the correspondence principle: (1) a rule—commonly attributed to Born (1924)¹⁸³ but found independently by both Kramers and Van Vleck (see below)—for replacing derivatives with respect to the action variables in classical formulae by difference quotients involving neighboring quantum states; (2) the A and B coefficients of Einstein's quantum theory of radiation. In general, the 'translation' of a classical formula into a quantum formula involves a third step. The orbital frequencies need to be replaced by transition frequencies. The case of a simple harmonic oscillator has the special features that the only relevant transitions are between adjacent states and that the transition frequency $\nu_{i \rightarrow f}$ coincides with the mechanical frequency ν_0 . Another special feature is that the correspondence between quantum and classical results for large quantum numbers continues to hold all the way down to the lowest quantum numbers, due to the extremely simple form of the energy spectrum, with uniformly spaced levels.

Using the rule for replacing derivatives by difference quotients, the quantum formula for polarization is obtained from (49) by the formal correspondence

¹⁸²For a discussion of infinitesimal canonical transformations, see Ch. 11 of (Matzner and Shepley, 1991).

¹⁸³See, e.g., (Jammer, 1966, p. 193), (MacKinnon, 1977, p. 148), (Cassidy, 1991, pp. 178, 186, 188), or (Aitchison *et al.*, 2004, p. 1372).

replacement

$$\left. \frac{\partial F(w, J)}{\partial J} \right|_{J=rh} \rightarrow \frac{1}{h}(F(r+1) - F(r)), \quad (54)$$

where F can be any dynamical quantity of the system. Classically, it is a function $F(w, J)$ on phase space. $F(r)$ denotes its value, $F(w, J = rh)$, in the quantum state specified by the integer quantum number r . In the correspondence limit where r gets very large, the difference between the values rh and $(r+1)h$ for the action variable J becomes so small that the difference quotient to the right of the arrow in eq. (54) approaches the derivative on the left. With this prescription, the classical formula eq. (49) turns into a quantum expression for the coherent part of the displacement of the particle in quantum state r :

$$\Delta x_{\text{coh}}^r = \frac{2eE}{h} \left(\frac{\nu_0 |A^{r+1}|^2}{\nu^2 - \nu_0^2} - \frac{\nu_0 |A^r|^2}{\nu^2 - \nu_0^2} \right) \cos 2\pi\nu t. \quad (55)$$

The amplitudes A^r correspond to the A_τ (with $\tau = \pm 1$) in eq. (49), and are related to the amplitudes D_r in eq. (32) for an oscillator in state r by $D_r = 2|A^r|$ (see eq. (51)). As we saw in sec. 3.3, Ladenburg (1921) showed how these amplitudes can be connected to the Einstein A coefficients for spontaneous emission (not to be confused with the amplitudes A^r).

At this point we briefly review Einstein's quantum theory of radiation (Einstein, 1916a,b, 1917), using the notation of (Van Vleck, 1924b). Imagine an ensemble of atoms—or indeed, any conceivable quantized mechanical system, such as one-dimensional quantized oscillators—in interaction and statistical equilibrium with an ambient electromagnetic field of spectral density $\rho(\nu)$. If we label the stationary states of the atoms by indices r, s, \dots , the number of atoms in state r (of energy E_r) by N_r , and recall the Bohr frequency condition $\nu_{rs} = (E_r - E_s)/h$, Einstein's analysis gives the average rate of energy emission of light of frequency ν_{rs} for an atom in state r as

$$\frac{dE_{r \rightarrow s}}{dt} = h\nu_{rs} (A_{r \rightarrow s} + B_{r \rightarrow s}\rho(\nu_{rs})), \quad (56)$$

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

$$\frac{dE_{s \rightarrow r}}{dt} = h\nu_{rs} B_{s \rightarrow r}\rho(\nu_{rs}), \quad (57)$$

where $A_{r \rightarrow s}$, $B_{r \rightarrow s}$, and $B_{s \rightarrow r}$ are the transition probabilities for spontaneous emission, stimulated emission, and absorption, respectively. Einstein's analy-

sis of the requirements for thermodynamic equilibrium and comparison with Planck's law of black-body radiation then yields the critical relations

$$B_{r \rightarrow s} = B_{s \rightarrow r} = \frac{c^3}{8\pi h \nu_{rs}^3} A_{r \rightarrow s}. \quad (58)$$

For a charged simple harmonic oscillator, the only allowed transitions amount to changes in the action by one unit of Planck's constant h , so there is only a single Einstein coefficient for spontaneous emission from the state $r + 1$, namely $A_{r+1 \rightarrow r}$. The correspondence principle dictates that we associate the rate of spontaneous energy emission for *high* quantum numbers,

$$\frac{dE_{r+1 \rightarrow r}}{dt} = h\nu_0 A_{r+1 \rightarrow r} \quad (59)$$

(cf. eq. (56), in the absence of external radiation) with the classical result for the power emitted by an accelerated (in this case, oscillating) charge, given by the Larmor formula (Jackson, 1975; Feynman *et al.*, 1964, Vol. 1, Ch. 32):

$$P = \frac{2}{3} \frac{e^2}{c^3} \dot{v}^2. \quad (60)$$

For an oscillator in state r , with $x(t) = D_r \cos \omega_0 t$, this becomes, for the instantaneous power emission P_r in state r

$$P_r = \frac{2}{3} \frac{e^2}{c^3} \omega_0^4 D_r^2 \cos^2 \omega_0 t, \quad (61)$$

the time average of which, $\frac{1}{3}(e^2/c^3)\omega_0^4 D_r^2$, then gives the desired connection between the amplitudes $D_r = 2|A^r|$ appearing in eq. (55) and the Einstein coefficient $A_{r+1 \rightarrow r}$ in the correspondence limit:

$$\begin{aligned} h\nu_0 A_{r+1 \rightarrow r} &= \frac{4}{3} \frac{e^2}{c^3} \omega_0^4 |A^{r+1}|^2 \\ |A^{r+1}|^2 &= \frac{3hc^3}{64\pi^4 e^2 \nu_0^3} A_{r+1 \rightarrow r}. \end{aligned} \quad (62)$$

Van Vleck (1924b) refers to this connection as the ‘‘correspondence principle for emission’’ (p. 333). Substituting the expression for $|A^{r+1}|^2$ in eq. (62) into eq. (55) for Δx_{coh}^r and multiplying by the charge $-e$ to obtain the dipole moment per oscillator and by the number density of oscillators n_{osc} , we arrive at the following result for the polarization induced by the electric field E :

$$P_r = 3 \frac{n_{\text{osc}} c^3}{32\pi^4} E \left(\frac{A_{r+1 \rightarrow r}}{\nu_0^2(\nu_0^2 - \nu^2)} - \frac{A_{r \rightarrow r-1}}{\nu_0^2(\nu_0^2 - \nu^2)} \right) \cos 2\pi \nu t. \quad (63)$$

Of course, for the special case of the ground state of the oscillator, $r = 0$, the second term in eq. (63) cannot be present. Ladenburg's quantum formula for dispersion accordingly only had the equivalent of the first term in eq. (63) (see eq. (8) in sec. 3.3). The full equation corresponds to eq. (5) in (Kramers, 1924a), and to eq. (17) in (Van Vleck, 1924b), except for a factor of 3, as we have not assumed random orientation of the oscillators (Van Vleck, 1924b, footnote 25).

One may easily guess that the corresponding formula for a more general, multiply-periodic system will take the form of (Van Vleck, 1924b, eq (17)), in analogy to (63):

$$P_r = 3 \frac{n_{\text{osc}} c^3}{32\pi^4} E \left(\sum_s \frac{A_{s \rightarrow r}}{\nu_{sr}^2 (\nu_{sr}^2 - \nu^2)} - \sum_t \frac{A_{r \rightarrow t}}{\nu_{rt}^2 (\nu_{rt}^2 - \nu^2)} \right) \cos 2\pi\nu t, \quad (64)$$

where the sum over s (resp. t) corresponds to states higher (resp. lower) than the state r , and where ν_{ij} is Van Vleck's notation for the transition frequency $\nu_{i \rightarrow j}$. In the correspondence limit where r is very large and neither s nor t differ much from r , the transition frequencies ν_{sr} and ν_{rt} become equal to the orbital frequencies in the orbits characterized by the values rh , sh , and th for the action variable J . For the harmonic oscillator, the sums in eq. (64) degenerate to a single term each (with $s = r + 1$, $t = r - 1$), and the transition frequencies ν_{sr} , ν_{rt} are all equal to the mechanical frequency ν_0 . In sec. 6.2 we shall present Van Vleck's derivation of eq. (64) in detail.

As we indicated above, there is some disagreement in the historical literature as to who was (or were) responsible for the key move in the construction of the quantum dispersion formula on the basis of the correspondence principle, viz. the replacement (54) of derivatives with respect to the action variable by difference quotients. Jammer (1966, p. 193) and Mehra and Rechenberg (1982–2001, Vol. 2, p. 173) suggest that Kramers got the idea from Born via Heisenberg. Dresden (1987, p. 222) makes it clear that Kramers found the rule before Born, but allows for the possibility that Born found it independently, as Kramers did not state the rule in his first *Nature* note (Kramers, 1924a), the only presentation of the Kramers dispersion formula that Born had seen when he wrote (Born, 1924). Van Vleck certainly discovered the replacement (54) of derivatives by difference quotients for himself. Since Van Vleck (1924a) announced the correspondence principle for absorption, which he could not have derived without this rule, in a paper submitted in April 1924, whereas (Born, 1924) was not received by *Zeitschrift für Physik* until June 1924, Van Vleck clearly could not have taken the rule from Born's paper. That Kramers, Van Vleck, and probably Born independently hit upon the same idea, underscores that the rule (54) for replacing derivatives by difference quotients is so natural that it readily comes to mind when one is trying to connect quantum-theoretical expressions to classical ones on the basis of the correspondence

principle.

Writing to Born in 1924, Van Vleck sounds slightly annoyed at Born’s insinuation that he, Van Vleck, did not realize that one needs to replace derivatives by difference quotients to get from classical to quantum-theoretical expressions. In the letter from which we already quoted in sec. 2.4, Born had written:

I am sending you my paper On Quantum Mechanics [Born, 1924], which pursues a goal similar to yours. While you limit yourself to the correspondence with high quantum numbers, I conversely aim for rigorous laws for arbitrary quantum numbers.¹⁸⁴

To which Van Vleck replied:

I have read with great interest your important, comprehensive article. There is, as you say, considerable similarity in the subject matter in your article and mine, especially as regards to dispersion¹⁸⁵ . . . As noted in your letter you mention more explicitly than do I the fact that formulas of the quantum theory result from those of the classical theory by replacing a derivative by a difference quotient. I have stressed the asymptotic connection of the two theories but I think it is clear in the content of my article that in the problems considered the classical and quantum formulas are connected as are derivatives and difference quotients.¹⁸⁶

As we already mentioned in sec. 1.2 (see note 17) and sec. 3.4 (note 101), Van Vleck used the correspondence principle—in particular, the replacement of derivatives by difference quotients—to *check* that quantum formulae merge with classical formulae in the limit of high quantum numbers, whereas Born wanted to use the principle to *construct* quantum formulae out of their classical counterparts. We sympathize with Van Vleck’s point in response to Born that the difference between the two approaches should not be exaggerated. Although Van Vleck could take the quantum formulae for emission and dispersion from (Ladenburg and Reiche, 1923) and (Kramers, 1924a), respectively, he had to construct his own quantum formula for absorption on the basis of Einstein’s quantum theory of radiation. The formula for absorption was undoubtedly easier to guess than the one for dispersion, which took the combined efforts of Ladenburg and Kramers (see secs. 3.3–3.4), but, given that Ladenburg and Reiche (1923) got it wrong, it was not completely trivial either

¹⁸⁴Born to Van Vleck, October 24, 1924 (AHQP).

¹⁸⁵Van Vleck seems to be talking here about (Van Vleck, 1924b,c), whereas Born was talking about (Van Vleck, 1924a). Born asked Van Vleck to send him “an offprint of your extensive calculations.” Van Vleck obliged: “As you requested, I am sending you under separate cover a reprint of Parts I and II of my computations,” presumably (Van Vleck, 1924b,c).

¹⁸⁶Van Vleck to Born, November 30, 1924 (AHQP).

(see sec. 5.3). Moreover, Van Vleck’s crucial insight that what matters is the differential absorption was guided by the analogy between the quantum and the classical case. In fact, as Van Vleck (1924a, p. 30) himself pointed out (in a passage we quoted in sec. 3.4), his insight that one needs to take into account the effects of “negative absorption” (stimulated emission) to arrive at a quantum absorption formula that merges with the classical absorption formula in the correspondence limit, is precisely analogous to the insight that one needs to add a term describing such effects to the Ladenburg dispersion formula to arrive at a quantum dispersion formula, the Kramers formula, that merges with the classical dispersion formula in the correspondence limit. As we also saw in sec. 3.4, Van Vleck formulated his correspondence principle of absorption before Kramers (1924a) published his dispersion formula. In short, Van Vleck knew perfectly well how to construct quantum formulae on the basis of correspondence considerations when he had to. And while it is true that Born put more emphasis on the constructive use of the correspondence principle, this did not lead Born to additional results of any consequence for subsequent developments. It was left to Heisenberg to show how one could use the correspondence principle as a guide not just to a few new formulae but to a whole new theory. In the aftermath of Heisenberg’s breakthrough, the Göttingen-Copenhagen attitude seems to have been that the correspondence principle had been the ladder that had allowed physicists to get from the old quantum theory to the new matrix mechanics, a ladder that in the safe possession of the new theory could be discarded. Interestingly, Van Vleck’s attitude toward the correspondence principle did not change. In early 1928 he published a paper the aim of which is described as follows in the introduction:

In studying the very significant statistical interpretation [of quantum mechanics], the writer at first experienced considerable difficulty in understanding how the quantum formulas for averages and probabilities merge into the analogous classical expressions in the region of large quantum numbers and also, of course, in the limit $h = 0$. In the present note we shall aim to trace through the asymptotic connection between the formulas of the two theories, which does not seem to have been adequately elucidated in existing papers (Van Vleck, 1928, p. 178).¹⁸⁷

Even post-*Umdeutung*, Van Vleck thus continued to think of the correspondence principle in terms of checking rather than constructing quantum formulae.

¹⁸⁷We are grateful to John Stachel for drawing our attention to this paper, in which Van Vleck introduced what has become known as the “Van Vleck determinant.”

5.3 Emission and absorption classically and quantum-theoretically in the special case of a simple harmonic oscillator

Before we present Van Vleck’s “correspondence principle for absorption” (for the special case of a simple harmonic oscillator), we gather some useful results from the classical theory of a charged oscillator (of natural frequency ν_0) coupled to a Maxwellian electromagnetic field. Such an oscillator (i) emits electromagnetic radiation of frequency ν_0 in the absence of an external field, (ii) absorbs energy from an applied electromagnetic field of frequency ν , and (iii) undergoes a net displacement coherent with an applied electromagnetic field (or “polarization”, analyzed above).

The Larmor formula (60) gives the power loss due to radiation by our charged harmonic oscillator. The energy loss of the oscillating system can be ascribed to a radiative reaction force given by

$$F_{\text{rad}} = \frac{2e^2}{3c^3}\ddot{v} \equiv m\tau_{\text{D}}\ddot{v}, \quad (65)$$

where we shall assume that the characteristic radiation damping time τ_{D} is very short in comparison to the mechanical period: $\omega_0\tau_{\text{D}} \ll 1$, so that radiation damping is very slow on the time scale of the mechanical oscillations of the system. The equation of motion of the oscillator (in the absence of external applied forces) now becomes

$$\dot{v} - \tau_{\text{D}}\ddot{v} + \omega_0^2x = 0. \quad (66)$$

To a good approximation, the coordinates and velocities of this system are still behaving as harmonic oscillations of frequency ω_0 so we may assume $\ddot{v} \simeq -\omega_0^2v$ in (66) and obtain

$$\ddot{x} + \tau_{\text{D}}\omega_0^2\dot{x} + \omega_0^2x = 0. \quad (67)$$

Inserting the *Ansatz* $x(t) = De^{-\alpha t}$ into equation (67), we find:

$$(\alpha^2 - \tau_{\text{D}}\omega_0^2\alpha + \omega_0^2)De^{-\alpha t} = 0. \quad (68)$$

Neglecting a term with $\tau_{\text{D}}^2\omega_0^4$ (recall that $\omega_0\tau_{\text{D}} \ll 1$, so that $\tau_{\text{D}}^2\omega_0^4 \ll \omega_0^2$),¹⁸⁸

¹⁸⁸Such terms are treated incorrectly in any event by the approximation leading to eq. (67).

we can rewrite the expression in parentheses as:

$$\left(\alpha - \frac{1}{2}\tau_D\omega_0^2 + i\omega_0\right)\left(\alpha - \frac{1}{2}\tau_D\omega_0^2 - i\omega_0\right). \quad (69)$$

It follows that:

$$\alpha \simeq \frac{1}{2}\tau_D\omega_0^2 \pm i\omega_0 \equiv \Gamma/2 \pm i\omega_0. \quad (70)$$

Thus, we have a solution of the form

$$x(t) = De^{-\Gamma t/2} \cos \omega_0 t, \quad (71)$$

from which the average rate of oscillator energy loss from the Larmor formula (60) at small times (i.e., when damping due to the $e^{-\Gamma t/2}$ factor can be ignored) is easily seen to be

$$-\frac{dE_{\text{osc}}}{dt} = \frac{e^2}{3c^3} D^2 \omega_0^4 = \frac{16\pi^4 e^2}{3c^3} D^2 \nu_0^4 \quad (72)$$

(where we used that $\dot{v} \simeq \omega_0^2 D$). The constant $\Gamma = \tau_D \omega_0^2$ is called the radiative decay constant. We emphasize again that the preceding discussion presupposes the narrow resonance limit, $\Gamma \ll \omega_0$. In terms of Γ , the basic equation of motion (67) can be written as

$$\ddot{x} + \Gamma \dot{x} + \omega_0^2 x = 0. \quad (73)$$

Now suppose that our charged oscillator is immersed in an ambient electromagnetic field, characterized by a spectral function (energy density per unit spectral interval) $\rho(\nu)$. As we are dealing with one-dimensional oscillators we shall simplify the discussion by assuming that only the x -component of the electric field is relevant as all the oscillators are so aligned. Then (using overbars to denote time averages) the average value of the electromagnetic energy density is (in Gaussian units) $(1/4\pi)\bar{\mathbf{E}}^2 = (3/4\pi)\bar{E}_x^2 = \rho(\nu)\Delta\nu$ in the frequency interval $(\nu, \nu + \Delta\nu)$. If $E_x = E \cos 2\pi\nu t$ we have $\bar{E}_x^2 = E^2/2$ so finally we have

$$E^2 = \frac{8\pi}{3} \rho(\nu) \Delta\nu. \quad (74)$$

The equation of motion (73) must be modified to include the coupling to the external field (switching back temporarily to angular frequencies, $\omega = 2\pi\nu$,

and using complex notation to encode amplitude and phase information):

$$\ddot{x} + \Gamma\dot{x} + \omega_0^2 x = \frac{eE}{m} e^{i\omega t} \equiv F_{\text{app}}/m, \quad (75)$$

and the average rate of energy absorption of the oscillator from the ambient field is simply the time average $\langle F_{\text{app}}\dot{x} \rangle$. This linear second order equation is solved by a sum of transients (i.e. solutions of the homogeneous equation: see eq. (73))

$$x_{\text{tr}}(t) = D e^{-\Gamma t/2} \cos \omega_0 t, \quad (76)$$

plus the following particular solution coherent with the applied perturbation

$$x_{\text{coh}}(t) = \text{Re} \frac{eE}{m} \frac{e^{i\omega t}}{\omega_0^2 - \omega^2 + i\Gamma\omega}, \quad (77)$$

so that the desired time average $\langle F_{\text{app}}\dot{x} \rangle = \langle F_{\text{app}}(\dot{x}_{\text{tr}} + \dot{x}_{\text{coh}}) \rangle$ giving the energy absorption rate becomes

$$\langle F_{\text{app}}\dot{x} \rangle = \langle eE \cos \omega t \frac{eE}{m} \text{Re} \left(\frac{i\omega e^{i\omega t}}{\omega_0^2 - \omega^2 + i\Gamma\omega} \right) \rangle. \quad (78)$$

Note that the transient part of the particle coordinate $x_{\text{tr}}(t)$ is *not* coherent with the applied field (we assume $\omega \neq \omega_0$), and therefore does not contribute to the time average of the energy absorption. This explains why the amplitude D of the oscillations is absent from the final result, which will instead depend only on the specific energy density of the ambient field. In other words, even though the charged particle may be executing very large amplitude oscillations $x_{\text{tr}}(t)$, the only part of the full coordinate $x(t)$ responsible for a nonvanishing average absorption is the part of the displacement $x_{\text{coh}}(t)$ induced by the applied field, which is proportional to E and does not involve the amplitude D . As we shall see below, the corresponding feature of the quantum calculation in the correspondence limit led Van Vleck to the very important realization that the net energy absorption involves a *difference* in the amount of absorption and stimulated emission as described in Einstein's quantum theory of radiation.

Only the cosine part of the complex exponential in eq. (78) will contribute to the time average. Using $\langle \cos^2 \omega t \rangle = 1/2$ and eq. (74), we find

$$\begin{aligned} \langle F_{\text{app}}\dot{x} \rangle &= \frac{e^2 E^2 \Gamma}{2m} \frac{\omega^2}{(\omega_0^2 - \omega^2)^2 + \Gamma^2 \omega^2} \\ &= \frac{4\pi e^2}{3m} \rho \left(\frac{\omega}{2\pi} \right) \Gamma \frac{\omega^2}{(\omega_0^2 - \omega^2)^2 + \Gamma^2 \omega^2} \frac{1}{2\pi} \Delta\omega \end{aligned} \quad (79)$$

for the energy absorption rate due to the ambient field in the frequency interval $(\nu, \nu + \Delta\nu) = (\omega, \omega + \Delta\omega)$. Since eq. (79) contains the electric field E squared, it is apparent that the generalization of this linear simple harmonic oscillator result to an arbitrary multiply-periodic system will require a second-order canonical perturbation theory calculation, which will necessarily be more involved than the corresponding classical polarization calculation, which only involves the electric field to the first order. In the case of interest, where $\Gamma \ll \omega_0$, the line resonance shape in eq. (79) is highly peaked around the resonance frequency ω_0 , so we may use the distributional limit

$$\frac{\epsilon}{x^2 + \epsilon^2} \rightarrow \pi\delta(x), \quad \epsilon \rightarrow 0 \quad (80)$$

with $x = \omega^2 - \omega_0^2$ and $\epsilon = \Gamma\omega$ to execute the integration over ω in eq. (79) and compute the total absorption rate:

$$\begin{aligned} \langle F_{\text{app}}\dot{x} \rangle &\approx \frac{2e^2}{3m} \int \rho\left(\frac{\omega}{2\pi}\right) \Gamma \frac{\pi}{\Gamma\omega} \omega^2 \delta(\omega^2 - \omega_0^2) d\omega \\ &= \frac{\pi e^2}{3m} \rho(\nu_0). \end{aligned} \quad (81)$$

This classical result is found in (Planck, 1921) (Van Vleck, 1924b, p. 339, note 12))¹⁸⁹ and gives the rate at which a classical charged oscillator gains energy when immersed in an ambient classical electromagnetic field.

In eq. (62) we found the connection in the limit of high quantum numbers between the Einstein A coefficients and the amplitudes $D_r = 2|A^r|$ of the mechanical motion in the emitting state r :

$$A_{r \rightarrow s} \simeq \frac{16\pi^4 e^2}{3hc^3} D_r^2 \nu_{rs}^3. \quad (82)$$

From the Einstein relation (58) this implies a corresponding result for the B -coefficients:

$$B_{r \rightarrow s} = B_{s \rightarrow r} = \frac{2\pi^3 e^2}{3h^2} D_r^2. \quad (83)$$

In the r -th quantized state of the oscillator, we have $J = rh$ so from eq. (32)

¹⁸⁹Van Vleck probably got the references to (Planck, 1921) from (Ladenburg and Reiche, 1923). Both (Van Vleck, 1924b, p. 339, note 12; p. 340, note 14) and (Ladenburg and Reiche, 1923, p. 588, note 19; p. 591, note 30) cite “equations (260) and (159)” and “section 158” in (Planck, 1921).

the corresponding amplitude D_r^{qu} of the *quantized* motion becomes

$$D_r^{\text{qu}} = \sqrt{\frac{r\hbar}{2\pi^2 m \nu_0}}, \quad (84)$$

and the quantum result for the A coefficients in the present case of a linear simple harmonic oscillator becomes

$$A_{r \rightarrow r-1} = \frac{8\pi^2 e^2 \nu_0^2 r}{3mc^3}, \quad (85)$$

while the quantum result for the B coefficients takes the form

$$B_{r \rightarrow r-1} = B_{r-1 \rightarrow r} = \frac{\pi e^2 r}{3hm\nu_0}. \quad (86)$$

The Einstein analysis of A and B coefficients makes it clear that at the quantum level we must consider what Van Vleck (1924b, p. 340) calls the “differential absorption rate”: the rate of energy absorption of the oscillator in state r going to state $r + 1$ via (57) *minus* the stimulated emission induced by the ambient field and causing the transition r to $r - 1$ (the B term in (56)). From eq. (86) we therefore have for the differential absorption rate of an oscillator in state r

$$\begin{aligned} \frac{dE_{\text{net}}}{dt} &= h\nu_0(B_{r \rightarrow r+1} - B_{r \rightarrow r-1})\rho(\nu_0) \\ &= h\nu_0(B_{r+1 \rightarrow r} - B_{r \rightarrow r-1})\rho(\nu_0) \\ &= h\nu_0(r + 1 - r)\frac{\pi e^2}{3hm\nu_0}\rho(\nu_0) \\ &= \frac{\pi e^2}{3m}\rho(\nu_0), \end{aligned} \quad (87)$$

which is precisely the classical result (81). Note that the dependence on the quantum state r (or classically, the amplitude of the motion D_r) has cancelled in the differential absorption rate, corresponding to the lack of coherence discussed previously between the transient and impressed motion.

Van Vleck derived this result in sec. 4 of his paper. He concluded:

We thus see that in the limiting case of large quantum numbers, where [eq. (86)] is valid, the classical value [in eq. (81)] for the rate of absorption of energy is nothing but the differential rate of absorption in the quantum theory. This connection of the classical and quantum differential absorption

we shall term the correspondence principle of absorption (Van Vleck, 1924b, p. 340).¹⁹⁰

In sec. 5, he generalized the result to arbitrary non-degenerate multiply-periodic systems.

Van Vleck's correspondence principle for 'differential absorption' (i.e., the excess of absorption over stimulated emission) also clarifies the correspondence principle for dispersion. As Kramers (1924a,b) emphasized, the negative terms in the dispersion formula were difficult to account for on the basis of purely classical concepts—they somehow corresponded to a *negative* value for e^2/m for those virtual oscillators corresponding to transitions from the initial atomic level to lower energy levels (see sec. 3.4). Similar negative contributions in the case of absorption are physically much more transparent: transitions to higher levels result in a positive absorption of energy from the ambient electromagnetic field, whereas transitions to lower levels result in energy being returned to the field. The latter process was therefore known as "negative absorption" at the time, a term used by both Kramers (1924a, p. 676) and Van Vleck (1924b, p. 338). Noticing the greater physical transparency of his correspondence-principle results for absorption, and under the impression that Kramers' correspondence-principle arguments for the dispersion formula rested only on a treatment of harmonic oscillators, Van Vleck added sections on dispersion to his paper. Sec. 6, "The general correspondence principle basis for Kramers dispersion formula," was added to the first quantum-theoretical part of the paper; sec. 15, "Computation of polarization," to the classical part (see the letter from Van Vleck to Kramers of September 1924, quoted in sec. 3.4).

When Kuhn in his AHQP interview with Van Vleck brought up the paper on the correspondence principle for absorption, Van Vleck said: "I think that was one of my better papers." "How did you get into that?," Kuhn wanted to know. Van Vleck told him:

Through a misunderstanding of something Gregory Breit [Van Vleck's colleague in Minnesota at the time] told me. He said that the net absorption was the difference between the fluctuations up and the fluctuations down, referred to some paper of—I think it was (Kretschmann)—but that was an entirely different thing. It was concerned with the fact that under certain phase relations the light did work on the atom and under certain phase relations the atom did work on the light. It was dealing essentially with statistical fluctuations. I misunderstood his remark and proceeded to try and

¹⁹⁰Van Vleck points out that this "is a purely mathematical consequence of the correspondence principle for emission, which was used in deriving [eq. (86)]" (ibid.). A few pages later, Van Vleck (1924b, p. 343) notes that he could also have done the reverse, deriving the correspondence principle for emission from that for absorption.

get the differential effect between the absorption up from a given stationary state and a[b]sorption going down.¹⁹¹

The paper Breit was referring to is presumably (Kretschmann, 1921). In this paper, Erich Kretschmann (1887–1973), a student of Planck better known for his work in general relativity (Kretschmann, 1917), gave a purely classical discussion of the emission and absorption of radiation. What Van Vleck says here about this paper fits with its contents.

Van Vleck’s comments, however, are also reminiscent of the following passage in (Ladenburg and Reiche, 1923):

... according to Einstein’s assumptions the effect of external radiation on a quantum atom corresponds to the effect a classical oscillator experiences from an incident wave. When the frequency of such a wave does not differ much or not at all from the characteristic frequency of the oscillator, the reaction of the oscillator consists in an increase or a decrease of its energy, depending on the difference in phase between the external wave and the motion of the oscillator. In analogy to this, Einstein assumes that the atom in state i has a probability characterized by the factor b_{ik} to make a transition to a higher state k under absorption of the energy $h\nu$ of the incident wave (“positive irradiation”) and that the atom in state k has another probability (b_{ki}) to return to the state i under the influence of an external wave (“negative irradiation”) (Ladenburg and Reiche, 1923, p. 586)

As we mentioned in sec. 3.3, Ladenburg and Reiche appealed to the correspondence principle to justify their quantum formulae for emission, absorption, and dispersion. Except in the case of emission, however, their arguments were fallacious. We conjecture that this is what inspired Van Vleck to use his expertise in techniques from celestial mechanics to find the correct expressions for emission and absorption merging with classical results in the sense of the correspondence principle.¹⁹² Van Vleck (1924b, p. 339, note 13; p. 344, note 21) cited Ladenburg and Reiche but gave no indication that their paper was an important source of inspiration for his own. It is not implausible, however, that Van Vleck simply preferred to pass over their badly flawed calculations

¹⁹¹P. 22 of the transcript of the first session of the AHQP interview with Van Vleck. Van Vleck told this story in somewhat greater detail to Katherine Sopka. He also explained to her why he acknowledged Breit in (Van Vleck, 1924a, p. 28) but not in (Van Vleck, 1924b,c): “As he [Van Vleck] remembers it, he wanted to thank Breit in the latter, but Breit objected on the ground that the phase fluctuations he had in mind were quite different from the difference effect employed by Van Vleck and so, overmodestly, felt no acknowledgment was in order” (Sopka, 1988, p. 135, note 184; this note makes no mention of Kretschmann).

¹⁹²As we saw in sec. 3.4, Van Vleck’s calculations for dispersion were inspired by (Kramers, 1924a).

in silence rather than touting his own clearly superior results. As we mentioned in sec. 3.3, one of the problems with the “correspondence” arguments of Ladenburg and Reiche is that, following (Planck, 1921) and in the spirit of the derivation of the A and B coefficients in (Einstein, 1917), they focus on collections of atoms in thermal equilibrium rather than on individual atoms. What is suggestive of a possible influence of (Ladenburg and Reiche, 1923) on (Van Vleck, 1924b,c) is that the exact same passages of (Planck, 1921) are cited in both papers (see note 189 above) and that Van Vleck (1924b) explicitly comments on the issue of many atoms in thermal equilibrium versus single atoms, noting that in Planck’s discussion “no explicit mention is made of the asymptotic connection of the classical absorption and the differential absorption for a single orbit (where thermodynamic equilibrium need not be assumed) which is the primary concern of the present paper” (p. 340, note 14). The topic of the third installment that Van Vleck originally planned to add to his two-part paper also becomes understandable in light of our conjecture about the connection between (Van Vleck, 1924b,c) and (Ladenburg and Reiche, 1923). As Van Vleck explained in 1977 (see sec. 2.4): “Part III was to be concerned with the equilibrium between absorption and emission under the Rayleigh-Jeans law” (Van Vleck and Huber, 1977, p. 939). If Ladenburg and Reiche did indeed stimulate Van Vleck’s work, however, it is somewhat puzzling that he does not seem to have recognized that the virtual oscillators of BKS, which, as we saw in secs. 3.4, 4.1, and 4.2, he consistently attributed to Slater, were essentially just the substitute oscillators of (Ladenburg and Reiche, 1923). We also saw, however, that Van Vleck was hardly alone in associating virtual oscillators with BKS. We thus conclude that it is plausible that Van Vleck was inspired by (Ladenburg and Reiche, 1923) to formulate correspondence principles for emission and absorption. For one thing, this would explain why Van Vleck, who had not worked on radiation theory before, turned his attention to the interaction between matter and radiation.

6 Generalization to arbitrary non-degenerate multiply-periodic systems

6.1 *The correspondence principle for absorption*

The primary result of (Van Vleck, 1924b,c) was an extension of eq. (87) to an arbitrary non-degenerate multiply-periodic system of a single particle in three dimensions, and the demonstration that the quantum-differential absorption coincides with this more general result in the correspondence limit. Before giving Van Vleck’s result we recall some basic features of multiply-periodic systems, which we shall in any event need in sec. 6.2, where we give a completely explicit derivation (following, with minor notational changes, the one

laid out by Van Vleck) of the corresponding formula for polarization.

The transition from one-dimensional periodic (and harmonic) systems such as the linear simple harmonic oscillator to three-dimensional multiply-periodic ones is fairly straightforward. Apart from the obvious need to introduce vector quantities, there are only two significant additional features. First, there is the appearance of multiple overtones in the general multiply-periodic expansion (so that the multiplicity variables in the analogue of eq. (34) take arbitrary positive and negative integral values, not just ± 1). Second, the mechanical frequencies ν_1, ν_2, ν_3 (with $\nu_i = \partial H_0 / \partial J_i$) of the separated coordinates are now in general functions of the amplitude of the classical path, which is to say, of the action variables J_i (with $i = 1, 2, 3$). We assume as before that the imposed electric field is in the X -direction so the x -coordinate of our electron is the relevant one for computing the induced coherent polarization, and in analogy to eq. (34) we now have

$$x(t) = \sum_{\vec{\tau}} A_{\vec{\tau}} e^{2\pi i \vec{\tau} \cdot \vec{w}}, \quad (88)$$

where in the absence of the external field the angle variables $\vec{w} = (w_1, w_2, w_3) = (\nu_1, \nu_2, \nu_3)t \equiv \vec{\nu}t$ and $\vec{\tau} = (\tau_1, \tau_2, \tau_3)$ with τ_i taking on all (positive and negative) integer values. It will be useful to write eq. (88) in an alternative purely real form, as a cosine expansion:

$$x(t) = \sum_{\vec{\tau}, \vec{\tau} \cdot \vec{\nu} > 0} X_{\vec{\tau}} \cos(2\pi \vec{\tau} \cdot \vec{\nu} t). \quad (89)$$

The complex amplitudes $A_{\vec{\tau}}$ satisfy the conjugacy condition $A_{\vec{\tau}} = A_{-\vec{\tau}}^*$ to ensure that $x(t)$ is real and we have the relation $X_{\vec{\tau}}^2 = 4A_{\vec{\tau}}A_{-\vec{\tau}}$.¹⁹³

As before (cf. eq. (33)), the full Hamiltonian has the form

$$H = H_0 + eEx(t) \cos 2\pi \nu t. \quad (90)$$

The subscripted mechanical frequencies ν_i with $i = 1, 2, 3$ (comprising the vector $\vec{\nu}$) must be distinguished from the single frequency ν (unsubscripted) corresponding to the applied field.

With these notations, Van Vleck's result for the absorption rate becomes (Van Vleck, 1924b, p. 342, eq. (16)):

$$\frac{dE_{\text{net}}}{dt} = \frac{2}{3} \pi^3 e^2 \left[\rho(\vec{\tau} \cdot \vec{\nu}) \tau_k \frac{\partial G_{\vec{\tau}}}{\partial J_k} + \rho'(\vec{\tau} \cdot \vec{\nu}) G_{\vec{\tau}} \tau_k \frac{\partial}{\partial J_k} (\vec{\tau} \cdot \vec{\nu}) \right]. \quad (91)$$

¹⁹³Cf. eqs. (34)–(35) and note 180 in sec. 6.1.

where $\rho' \equiv \partial\rho/\partial\nu$ and where summation over $k = (1, 2, 3)$ is implied and where $G_\tau \equiv \vec{\tau} \cdot \vec{\nu} D_\tau^2$ with $D_\tau^2 \equiv X_\tau^2 + Y_\tau^2 + Z_\tau^2$. In the special case of the harmonic oscillator, the term with ρ' , the derivative of the spectral function, vanishes as there is only a single mechanical frequency $\nu = \nu_0$, which is independent of the action variable J . In the first term, we get simply

$$\frac{dE_{\text{net}}}{dt} = \frac{2}{3}\pi^3 e^2 \rho(\nu_0) \frac{\partial}{\partial J} (\nu_0 D^2). \quad (92)$$

Using eq. (32), $D = \sqrt{J/m\pi\omega_0}$, for the amplitude, we recover the previous result, eq. (87).

Eq. (91) is the product of a highly nontrivial application of canonical perturbation techniques, where quantities of *second* order in the applied field need to be properly evaluated (cf. discussion following eq. (79) above). The polarization calculation presented in full in the sec. 6.2 only involves canonical perturbation theory to first order. For the absorption calculation, the variation in the action variables ΔJ_k in particular is needed to second order, and the integration of the result obtained for a monochromatic incident field needed to pass to the case of continuous radiation specified by an arbitrary spectral function $\rho(\nu)$ requires considerable care.

Slater also tried his hand at this calculation, as can be inferred from a letter from Kramers to Van Vleck, from which we already quoted in sec. 3.4. Kramers wrote:

Slater had, on my request, made the same calculation, and he stated that the classical mean-absorption formula gave the right result in the limit of high quantum numbers. I did, however, not see his formula, and am not quite sure that he had not forgotten the term with $\partial\rho/\partial\nu$, without which the thing is not complete of course.¹⁹⁴

Van Vleck clearly remembered this point almost forty years later. Talking to Kuhn about his 1924 absorption papers, he mentioned: “I got the term in partial rho with respect to nu. I’m very proud of the fact that I picked that one up . . . Slater, at Kramers’ suggestion I guess, made a completely parallel calculation in Copenhagen which he never published.”¹⁹⁵

¹⁹⁴Kramers to Van Vleck, November 11, 1924 (AHQP).

¹⁹⁵P. 22 of the transcript of the first session of the AHQP interview with Van Vleck.

6.2 The correspondence principle for polarization

In this section we retrace the derivation given by Van Vleck (1924c) of the classical polarization formula for a general non-degenerate multiply-periodic system (with a single electron) in three dimensions. We remind the reader that this result is by no means new to Van Vleck, nor, for that matter, to Born or Kramers, who also produced derivations of the same result at around this time, using slightly different versions of canonical perturbation theory (cf. our comments at the end of sec. 6.1). The formula obtained is basically identical to a formula originally derived in celestial mechanics to compute the perturbation in the orbits of the inner planets due to the outer ones. As we saw in sec. 3.2, Epstein had been the first to use the relevant techniques from celestial mechanics in the context of the old quantum theory. As Van Vleck reminded Slater: “The classical formula analysis to the Kramer[s] formula appears to be first calculated by Epstein [1922c].”¹⁹⁶

The derivation is basically a straightforward generalization of the derivation of sec. 5.1 for the special case of a charged simple harmonic oscillator in an electromagnetic field (see eqs. (37)–(49)). The first-order perturbation in the coordinate $x(t)$ (the direction of the electric field in the incident electromagnetic wave) corresponding to the shifts $(\Delta J_l, \Delta w_l)$ in the action-angle variables is given by the three-dimensional version of eq. (37):

$$\Delta x = \sum_l \left(\frac{\partial x}{\partial J_l} \Delta J_l + \frac{\partial x}{\partial w_l} \Delta w_l \right). \quad (93)$$

As in sec. 5.1, we imagine that the external field is switched on at time zero, so that the shifts $(\Delta J_l, \Delta w_l)$ are the integrals of their time derivatives from 0 to t . In analogy with eq. (42) and using eq. (88) for $x(t)$, we can immediately write down the equation for ΔJ_l to first order in E :

$$\Delta J_l = \int_0^t \dot{J}_l dt = \frac{eE}{2} \sum_{\vec{\tau}} \tau_l A_{\vec{\tau}} \left\{ \frac{1 - e^{2\pi i(\vec{\tau} \cdot \vec{\nu} + \nu)t}}{\vec{\tau} \cdot \vec{\nu} + \nu} + (\nu \rightarrow -\nu) \right\}. \quad (94)$$

All the terms inside the summation can be taken to zeroth order in the applied field. The computation of the first-order shifts Δw_l is a little more involved as new terms, not present in the harmonic-oscillator case, enter (cf. note 181). The Hamilton equation for \dot{w}_l for the full Hamiltonian eq. (90) is (cf. eq. (43)):

$$\dot{w}_l = \nu_l + \frac{eE}{2} \sum_{\vec{\tau}} \frac{\partial A_{\vec{\tau}}}{\partial J_l} \left\{ e^{2\pi i(\vec{\tau} \cdot \vec{\nu} + \nu)t} + (\nu \rightarrow -\nu) \right\}. \quad (95)$$

¹⁹⁶Van Vleck to Slater, December 15, 1924 (AHQP).

Both terms in eq. (95) contribute to the first-order deviation $\Delta\dot{w}_l$ from the value of ν_l for the unperturbed system. Since ν_l depends on J_k , there will be a term $\sum_k(\partial\nu_l/\partial J_k)\Delta J_k$ (cf. note 181). The second term is just the generalization of the corresponding term in eq. (43). Hence, we get:

$$\Delta\dot{w}_l = \sum_k \frac{\partial\nu_l}{\partial J_k} \Delta J_k + \frac{eE}{2} \sum_{\vec{\tau}} \frac{\partial A_{\vec{\tau}}}{\partial J_l} \left\{ e^{2\pi i(\vec{\tau}\cdot\vec{\nu}+\nu)t} + (\nu \rightarrow -\nu) \right\}. \quad (96)$$

Upon substitution of eq. (94) for ΔJ_k this turns into

$$\Delta\dot{w}_l = \frac{eE}{2} \sum_{\vec{\tau},k} \left\{ \frac{\partial A_{\vec{\tau}}}{\partial J_l} e^{2\pi i(\vec{\tau}\cdot\vec{\nu}+\nu)t} + \tau_k \frac{\partial\nu_l}{\partial J_k} A_{\vec{\tau}} \frac{1 - e^{2\pi i(\vec{\tau}\cdot\vec{\nu}+\nu)t}}{\vec{\tau}\cdot\vec{\nu} + \nu} \right\} + (\nu \rightarrow -\nu). \quad (97)$$

Integrating eq. (97), we find

$$\Delta w_l = \frac{eE}{4\pi} \sum_{\vec{\tau},k} \left\{ i \frac{\partial A_{\vec{\tau}}}{\partial J_l} \frac{1 - e^{2\pi i(\vec{\tau}\cdot\vec{\nu}+\nu)t}}{\vec{\tau}\cdot\vec{\nu} + \nu} + \tau_k \frac{\partial\nu_l}{\partial J_k} A_{\vec{\tau}} \frac{2\pi(\vec{\tau}\cdot\vec{\nu} + \nu)t - i(1 - e^{2\pi i(\vec{\tau}\cdot\vec{\nu}+\nu)t})}{(\vec{\tau}\cdot\vec{\nu} + \nu)^2} \right\} + (\nu \rightarrow -\nu). \quad (98)$$

Inserting eq. (88) into eq. (93), we arrive at

$$\Delta x(t) = \sum_{\vec{\tau}',l} \left(\frac{\partial A_{\vec{\tau}'}}{\partial J_l} \Delta J_l + 2\pi i A_{\vec{\tau}'} \tau'_l \Delta w_l \right) e^{2\pi i \vec{\tau}' \cdot \vec{\nu} t}. \quad (99)$$

Inserting eqs. (94) and (98) for ΔJ_l and Δw_l , respectively, into this expression, we obtain

$$\Delta x(t) = \frac{eE}{2} \sum_{\vec{\tau}',\vec{\tau},k,l} \left\{ \tau_l \frac{\partial A_{\vec{\tau}'}}{\partial J_l} A_{\vec{\tau}} \frac{1 - e^{2\pi i(\vec{\tau}\cdot\vec{\nu}+\nu)t}}{\vec{\tau}\cdot\vec{\nu} + \nu} - \tau'_l \frac{\partial A_{\vec{\tau}'}}{\partial J_l} A_{\vec{\tau}'} \frac{1 - e^{2\pi i(\vec{\tau}\cdot\vec{\nu}+\nu)t}}{\vec{\tau}\cdot\vec{\nu} + \nu} + A_{\vec{\tau}} A_{\vec{\tau}'} \tau_k \frac{\partial\nu_l}{\partial J_k} \tau'_l \frac{2\pi i(\vec{\tau}\cdot\vec{\nu} + \nu)t + 1 - e^{2\pi i(\vec{\tau}\cdot\vec{\nu}+\nu)t}}{(\vec{\tau}\cdot\vec{\nu} + \nu)^2} + (\nu \rightarrow -\nu) \right\} e^{2\pi i \vec{\tau}' \cdot \vec{\nu} t}. \quad (100)$$

As in sec. 5.1, we are only interested in the coherent contribution to the polarization, so we drop all terms in eq. (100) whose time dependence is not precisely $e^{\pm 2\pi i \nu t}$ and find, writing for convenience $\sum_k \tau_k (\partial/\partial J_k) \equiv \vec{\tau} \cdot \vec{\nabla}_J$,

$$\Delta x_{\text{coh}} = \frac{eE}{2} \sum_{\vec{\tau}} \left\{ -\vec{\tau} \cdot \vec{\nabla}_J (A_{\vec{\tau}} A_{-\vec{\tau}}) \frac{e^{2\pi i \nu t}}{\vec{\tau} \cdot \vec{\nu} + \nu} \right. \\ \left. + A_{\vec{\tau}} A_{-\vec{\tau}} \vec{\tau} \cdot \vec{\nabla}_J (\vec{\tau} \cdot \vec{\nu}) \frac{e^{2\pi i \nu t}}{(\vec{\tau} \cdot \vec{\nu} + \nu)^2} \right\} + (\nu \rightarrow -\nu). \quad (101)$$

Note that the coherent contribution derives from terms in which $\vec{\tau}' = -\vec{\tau}$, as otherwise the uncanceled overtones from the mechanical system would shift the spectral line (as in Raman scattering). Essentially the only additional physics of (Kramers and Heisenberg, 1925) in comparison to (Van Vleck, 1924b,c) is a detailed examination of such terms, predicted earlier by Smekal (1923). The terms in eq. (101) involving $\sin 2\pi\nu t$ vanish, as can be seen with the help of the identities

$$\sum_{\vec{\tau}} \tau_j \left(\frac{1}{\vec{\tau} \cdot \vec{\nu} + \nu} - \frac{1}{\vec{\tau} \cdot \vec{\nu} - \nu} \right) \cdot (\text{even function of } \vec{\tau}) = 0 \\ \sum_{\vec{\tau}} \tau_j \tau_k \left(\frac{1}{(\vec{\tau} \cdot \vec{\nu} + \nu)^2} - \frac{1}{(\vec{\tau} \cdot \vec{\nu} - \nu)^2} \right) \cdot (\text{even function of } \vec{\tau}) = 0.$$

Thus eq. (101) simplifies to

$$\Delta x_{\text{coh}} = -\frac{eE}{2} \cos 2\pi\nu t \sum_{\vec{\tau}} \left\{ \vec{\tau} \cdot \vec{\nabla}_J \left(\frac{A_{\vec{\tau}} A_{-\vec{\tau}}}{\vec{\tau} \cdot \vec{\nu} + \nu} \right) + (\nu \rightarrow -\nu) \right\} \\ = -eE \cos 2\pi\nu t \sum_{\vec{\tau}} \vec{\tau} \cdot \vec{\nabla}_J \left(\frac{\vec{\tau} \cdot \vec{\nu} A_{\vec{\tau}} A_{-\vec{\tau}}}{(\vec{\tau} \cdot \vec{\nu})^2 - \nu^2} \right). \quad (102)$$

With the replacement $X_{\vec{\tau}}^2 = 4A_{\vec{\tau}}A_{-\vec{\tau}}$, we may go over to the cosine form of the expansion in eq. (102) (cf. eqs. (88)–(89)), summing over only positive values of $\vec{\tau} \cdot \vec{\nu}$ (with a factor of 2):

$$\Delta x_{\text{coh}} = -\frac{eE}{2} \cos 2\pi\nu t \sum_{\vec{\tau}, \vec{\tau} \cdot \vec{\nu} > 0} \vec{\tau} \cdot \vec{\nabla}_J \left(\frac{\vec{\tau} \cdot \vec{\nu} X_{\vec{\tau}}^2}{(\vec{\tau} \cdot \vec{\nu})^2 - \nu^2} \right). \quad (103)$$

This is the generalization of eq. (49) for the harmonic oscillator.

Finally, we obtain the polarization by multiplying the displacement by N_r , the number of electrons per unit volume (the subscript r refers to the fact that we shall shortly consider only electrons in a particular quantum state r), and by $-e$ for the electron charge

$$P = N_r \frac{e^2}{2} E \cos 2\pi\nu t \sum_{\vec{\tau}, \vec{\tau} \cdot \vec{\nu} > 0} \vec{\tau} \cdot \vec{\nabla}_J \left(\frac{\vec{\tau} \cdot \vec{\nu} X_{\vec{\tau}}^2}{(\vec{\tau} \cdot \vec{\nu})^2 - \nu^2} \right) \quad (104)$$

which is eq. (41) in (Van Vleck, 1924c; in Van Vleck's notation, $\vec{\tau} \cdot \vec{\nu}$ is written ω_τ) and equivalent to eq. 2* in (Kramers, 1924b) (see eq. (50) above).

The equivalence of eq. (104) to the Kramers dispersion formula (64) in the correspondence limit is sketched in (Kramers, 1924b) and fully explained in sec. 6 of (Van Vleck, 1924b).¹⁹⁷ Here we follow the latter. So we begin with eq. (64) for the polarization of a quantized system in state r , without the factor of 3 corresponding to the assumption that all oscillators be aligned with the applied field (rather than randomly in 3 dimensional space), and writing N_r instead of n_{osc} :

$$P_r = \frac{N_r c^3}{32\pi^4} E \cos 2\pi\nu t \left(\sum_s \frac{A_{s \rightarrow r}}{\nu_{sr}^2 (\nu_{sr}^2 - \nu^2)} - \sum_t \frac{A_{r \rightarrow t}}{\nu_{rt}^2 (\nu_{rt}^2 - \nu^2)} \right). \quad (105)$$

The sums over s (resp. t) refer to states higher (resp. lower) in energy than the fixed state r under consideration. In the correspondence limit, we take the state r to correspond to very high quantum numbers (n_1, n_2, n_3) . The states s, t are associated to the central state r in symmetrical pairs:

$$\begin{aligned} s &\rightarrow (n_1 + \tau_1, n_2 + \tau_2, n_3 + \tau_3), \\ r &\rightarrow (n_1, n_2, n_3), \\ t &\rightarrow (n_1 - \tau_1, n_2 - \tau_2, n_3 - \tau_3), \end{aligned} \quad (106)$$

with $\vec{\tau} \cdot \vec{\nu} > 0$ so that the states s (resp. t) do indeed correspond to higher (resp. lower) energy states. Furthermore, we assume that $\vec{\tau} \cdot \vec{\nu} \ll \vec{n} \cdot \vec{\nu}$ so that the transitions $s \rightarrow r \rightarrow t$ correspond to very slight changes in the classical orbitals (and differences approximate well to derivatives). The Bohr-Sommerfeld quantization condition (1) associates action values $J_i = n_i h$ with a given quantized state, so the formal correspondence principle becomes (cf. eq. (54) in sec. 6.2):

$$\delta_{\vec{\tau}} F(\vec{n}) \equiv F(\vec{n}) - F(\vec{n} - \vec{\tau}) \rightarrow h \vec{\tau} \cdot \vec{\nabla}_{\vec{J}} F. \quad (107)$$

In this notation, formula (105) the polarization can be written as

$$P_r = \frac{N_r c^3}{32\pi^4} E \cos 2\pi\nu t \sum_{\vec{\tau}} \delta_{\vec{\tau}} \left(\frac{A_{s \rightarrow r}}{\nu_{sr}^2 (\nu_{sr}^2 - \nu^2)} \right), \quad (108)$$

with $A_{s \rightarrow r}$ given by Van Vleck's "correspondence principle for emission" (see

¹⁹⁷Cf. Van Vleck to Kramers, September 22, 1924 (AHQP), quoted in sec. 3.4.

eq. (82) and eq. (62))

$$A_{s \rightarrow r} = \frac{16\pi^4 e^2}{3hc^3} D_s^2 \nu_{sr}^3, \quad (109)$$

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 $\vec{n} + \vec{\tau} \rightarrow \vec{n}$. Substituting eqs. (107) and (109) into eq. (108) and replacing the difference frequency ν_{sr} by its classical counterpart $\vec{\tau} \cdot \vec{\nu}$, we obtain, :

$$\begin{aligned} P_r &= N_r E \cos 2\pi\nu t \frac{c^3}{32\pi^4} \frac{16\pi^4 e^2}{3hc^3} h \sum_{\vec{\tau} \cdot \vec{\nu} > 0} \vec{\tau} \cdot \vec{\nabla}_J \left(\frac{\vec{\tau} \cdot \vec{\nu} D_s^2}{(\vec{\tau} \cdot \vec{\nu})^2 - \nu^2} \right) \\ &= N_r \frac{e^2}{2} E \cos 2\pi\nu t \sum_{\vec{\tau} \cdot \vec{\nu} > 0} \vec{\tau} \cdot \vec{\nabla}_J \left(\frac{\vec{\tau} \cdot \vec{\nu} \frac{1}{3} D_s^2}{(\vec{\tau} \cdot \vec{\nu})^2 - \nu^2} \right). \end{aligned} \quad (110)$$

With the replacement $\frac{1}{3} D_s^2 \rightarrow X_{\vec{\tau}}^2$ appropriate for randomly oriented atoms, eq. (110) becomes identical to the classical formula (104). This shows that the Kramers dispersion formula (105) does indeed merge with the classical result in the limit of high quantum numbers, as Van Vleck set out to demonstrate.

7 Derivation of the formulae for dispersion, emission, and absorption in modern quantum mechanics

Describing the impact of the new quantum mechanics on dispersion theory, Van Vleck wrote in 1929:

Dispersion was particularly bothersome in the old quantum theory, which could never explain why the resonance frequencies in dispersion were experimentally the spectroscopic frequencies given by the Bohr frequency condition rather than the altogether different frequencies of motion in orbits constituting the stationary states [cf. our discussion in the introduction of sec. 3]. The new mechanics, however, yields the Kramers dispersion formula, previously derived semi-empirically from the correspondence principle . . . As the result of the masterful treatment by Dirac [1927], a mechanism has at last to a certain extent been found for the previously so mysterious quantum jumps between stationary states (Van Vleck, 1929, pp. 494–495).

That same year, in the first installment of what would turn out to be an eight-part paper entitled “Investigations of anomalous dispersion in excited gases,” Ladenburg likewise provided a brief synopsis of recent developments in dispersion theory:

The first successful treatment of dispersion phenomena on the basis of Bohr's atomic theory implicitly contained the assumption that the orbital frequencies of the Bohr electrons are the special values at which dispersion changes sign.¹⁹⁸ In contrast to this, the point of departure of the *newer* development of dispersion theory is the empirical fact that not the orbital frequencies of the electrons but the frequencies, observable in emission and absorption, of "quantum jumps," i.e., spectral lines, are the singular values of anomalous dispersion. These correspond to the characteristic frequencies of quasi-elastically bound electrons in the classical electron theory [discussed in sec. 3.1]. Tying together the notions of this theory with Bohr's atomic theory has taught us that the "strength" of the dispersion or of the "substitute oscillators," which at Bohr's suggestion were introduced as carriers of the scattered radiation needed for dispersion, is determined in non-classical fashion by the "strength," i.e., the probability of quantum jumps[,] and by the density of atoms in the "lower" atomic state involved in such quantum jumps.¹⁹⁹ H. A. Kramers then showed,²⁰⁰ through correspondence considerations, that the dispersion formula obtained by the author [cf. eq. (8) in sec. 3.3] only holds exactly in the case of non-excited or meta-stable atoms; in the case of excited non-meta-stable atoms, which can also make spontaneous transitions to states of lower energy, this formula is incomplete and has to be supplemented by terms of "negative dispersion," which correspond to the "negative absorption" [i.e., stimulated emission] of the radiation theory of Planck and Einstein. Thus originated the "quantum-theoretical dispersion formula" [cf. eq. (9) in sec. 3.4] which has finally been given a fully consistent foundation in quantum mechanics and wave mechanics;²⁰¹ this new quantum theory completely avoids concepts like orbital frequencies of electrons in stationary states, and one of its points of departure was precisely the quantum-theoretical interpretation of dispersion phenomena mentioned above (Ladenburg, 1928, pp. 15–16)

Rather than pursuing the history of dispersion post-*Umdeutung*, we shall present our own modern derivations of quantum formulae for dispersion (sec. 7.1), (spontaneous) emission (sec. 7.2), and absorption (sec. 7.3). Seeing how modern quantum mechanics sanctions the formulae found by Kramers, Van

¹⁹⁸At this point, Ladenburg refers to the papers by Sommerfeld, Debye, and Davisson and the criticism of them by Bohr and Epstein that we discussed in sec. 3.2.

¹⁹⁹At this point, Ladenburg refers to his own work, Bohr's favorable reaction to it, and his subsequent work with Reiche, all discussed in sec. 3.3.

²⁰⁰At this point, Ladenburg refers to Kramers' two *Nature* notes and to the Kramers-Heisenberg paper discussed in sec. 3.4.

²⁰¹At this point, Ladenburg refers to the treatments of dispersion in (Born, Heisenberg, and Jordan, 1925, pp. 330–338) [see also (Born and Jordan, 1930, pp. 240–250)], (Schrödinger, 1926), and (Dirac, 1927). For discussion of Schrödinger's wave-mechanical treatment of dispersion, see (Mehra and Rechenberg, 1982–2001, Vol. 5, pp. 789–796).

Vleck and others in the old quantum theory on the basis of Einstein's quantum theory of radiation and Bohr's correspondence principle will illuminate various aspects of the relation between the old and the new theory.

First, we show how the orchestra of virtual oscillators of pre-*Umdeutung* dispersion theory survives in the guise of a sum over matrix elements of the position operator. Second, we show how the diagonal matrix elements of the fundamental commutation relation for position and momentum, $[X, P] = i\hbar$, are given by the high-frequency limit of the Kramers dispersion formula, a formula known as the Thomas-Kuhn(-Reiche) sum rule (Thomas, 1925; Kuhn, 1925; Reiche and Thomas, 1925). This formula replaces the Bohr-Sommerfeld condition as the fundamental quantization condition in the *Umdeutung* paper (see sec. 3.5). Heisenberg obtained the sum rule by applying the procedure introduced in the *Umdeutung* paper for translating classical quantities into quantum-theoretical ones to (a derivative of) the Bohr-Sommerfeld quantization condition. He then showed that the sum rule also obtains by comparing the high-frequency limit of the Kramers dispersion formula with the polarization of a charged harmonic oscillator in the limit where $\nu \gg \nu_0$ (see our eq. (53)). In hindsight, we can see clearly in the *Umdeutung* paper how close Heisenberg came to recognizing the presence of the commutation relation between position and momentum in the sum rule serving as his quantization condition. As he told Kuhn:

I had written down, as the quantization rule the Thomas-Kuhn sum rule, but I had not recognized that this was just pq minus qp. That I had not seen.²⁰²

That he did not take this step is probably due to two important obstacles, one conceptual, the other technical. The conceptual framework of the entire *Umdeutung* paper is Lagrangian (as opposed to Hamiltonian): the essential problem is to find a quantum-theoretical reinterpretation of the classical concepts of position $x(t)$ and *velocity* $\dot{x}(t)$ of a particle. Indeed, the conventional symbol for momentum, p , appears only *once* in the entire paper, in the statement of the Bohr-Sommerfeld quantization condition (eq. (12) in the paper). From this point on, p is replaced everywhere by $m\dot{x}(t)$. The canonical connection between position and momentum (so central, ironically, to the canonical perturbation theory that led to the dispersion formula in the first place²⁰³) seems simply to have vanished from Heisenberg's thinking at this point. The other, technical, obstacle was an inconvenient division of the sum over quantum states in the sum rule, which, though very natural from the point of

²⁰²P. 12 of the transcript of session 5 of the AHQP interview with Heisenberg. See also p. 9 of the transcript of session 7. Cf. our discussion in sec. 3.5. Heisenberg obtained his result by computing $(\oint pdq)_{n+1} - (\oint pdq)_n$.

²⁰³Of course, it was also central to (Dirac, 1925).

dispersion theory, obscured its connection to a commutator, as we shall see below.

It will also become clear in the course of our modern derivation that the Kramers dispersion formula is an even more general result in modern quantum mechanics than it was in the old quantum theory. In the old quantum theory, it held for any non-degenerate multiply-periodic system with an unperturbed Hamiltonian such that the unperturbed motion can be solved in action-angle variables. In modern quantum mechanics, the result holds for any system with a Hermitian Hamilton operator such that the unperturbed part has a spectrum that is at least partially discrete. This helps to explain why the Kramers dispersion formula carries over completely intact from the old quantum theory to modern quantum mechanics.

7.1 Dispersion

In this subsection, we derive the Kramers dispersion formula in time-dependent perturbation theory. We then examine the high-frequency limit of this formula and discuss the role it played in (Heisenberg, 1925) as the fundamental quantization condition replacing the Bohr-Sommerfeld condition.

We consider a quantized charged system (valence electron) with states labeled by discrete indices r, s, t, \dots , and with the Hamilton operator

$$H = H_0 + V(t) = H_0 + eEx \cos \omega t. \quad (111)$$

We want to calculate the first-order perturbation (in the electric field E) in the expectation value of the electron position in a particular state $|r, t\rangle$. It is convenient to work in the interaction picture.²⁰⁴ The state $|r, t\rangle_{\text{int}}$ in the interaction picture is related to the state $|r, t\rangle$ in the Schrödinger picture via:

$$|r, t\rangle_{\text{int}} \equiv e^{iH_0 t/\hbar} |r, t\rangle. \quad (112)$$

An operator $O_{\text{int}}(t)$ in the interaction picture is related to the corresponding operator O in the Schrödinger picture via

$$O_{\text{int}}(t) \equiv e^{iH_0 t/\hbar} O e^{-iH_0 t/\hbar}. \quad (113)$$

²⁰⁴The special role of H_0 in the time dependence of states and operators in the interaction picture is analogous to the choice of action-angle variables for the free rather than the full Hamiltonian in the version of canonical perturbation theory used by Van Vleck. This is what lies behind the close similarities between the calculations in this section and those in secs. 5.1 and 6.2.

It follows that expectation values are the same in the two pictures:

$${}_{\text{int}}\langle r, t | O_{\text{int}}(t) | r, t \rangle_{\text{int}} = \langle r, t | O | r, t \rangle. \quad (114)$$

The evolution of the states in the interaction picture is given by:

$$\begin{aligned} \frac{\partial}{\partial t} |r, t\rangle_{\text{int}} &= \frac{i}{\hbar} e^{iH_0 t/\hbar} H_0 |r, t\rangle + e^{iH_0 t/\hbar} \frac{\partial}{\partial t} |r, t\rangle \\ &= \frac{i}{\hbar} e^{iH_0 t/\hbar} (H_0 - H) |r, t\rangle, \end{aligned} \quad (115)$$

where in the last step, we used the Schrödinger equation

$$\frac{\partial}{\partial t} |r, t\rangle = -\frac{iH}{\hbar} |r, t\rangle. \quad (116)$$

Since $H_0 - H = -V(t)$ (see eq. (111)), we can write eq. (115) as:

$$\begin{aligned} \frac{\partial}{\partial t} |r, t\rangle_{\text{int}} &= -\frac{i}{\hbar} e^{iH_0 t/\hbar} V(t) e^{-iH_0 t/\hbar} |r, t\rangle_{\text{int}} \\ &= -\frac{i}{\hbar} V_{\text{int}}(t) |r, t\rangle_{\text{int}}, \end{aligned} \quad (117)$$

where we used eqs. (112)–(113). To first order in $V_{\text{int}}(t)$ (i.e., to first order in the field E), the solution of (117) is

$$\begin{aligned} |r, t\rangle_{\text{int}} &= |r, 0\rangle_{\text{int}} - \frac{i}{\hbar} \int_0^t d\tau V_{\text{int}}(\tau) |r, 0\rangle_{\text{int}} \\ &= |r, 0\rangle_{\text{int}} - \frac{ieE}{\hbar} \int_0^t d\tau x_{\text{int}}(\tau) \cos \omega\tau |r, 0\rangle_{\text{int}}. \end{aligned} \quad (118)$$

At $t = 0$ the states (and operators) in the interaction picture coincide with those in the Schrödinger picture. From now on we thus simply write $|r\rangle$ for $|r, 0\rangle_{\text{int}}$. The dual (‘bra’) of the vector (‘ket’) in eq. (118) is:

$${}_{\text{int}}\langle r, t | = \langle r | + \frac{ieE}{\hbar} \int_0^t d\tau \cos \omega\tau \langle r | x_{\text{int}}(\tau). \quad (119)$$

To find the dipole moment $P_r(t)$ of the system in state r to first order in E , we calculate the first-order contribution to the expectation value of the displacement $\langle \Delta x \rangle_r$ in the state r induced by the field E :

$$\langle \Delta x \rangle_r \equiv {}_{\text{int}}\langle r, t | x_{\text{int}}(t) | r, t \rangle_{\text{int}} - \langle r | x_{\text{int}}(t) | r \rangle. \quad (120)$$

Inserting eqs. (118)–(119) into this expression, we find:

$$\langle \Delta x \rangle_r = \frac{ieE}{\hbar} \int_0^t d\tau \langle r | \{x_{\text{int}}(\tau)x_{\text{int}}(t) - x_{\text{int}}(t)x_{\text{int}}(\tau)\} | r \rangle \cos \omega\tau. \quad (121)$$

Writing $\cos \omega\tau = \frac{1}{2}(e^{i\omega\tau} + e^{-i\omega\tau})$, and inserting a complete set of eigenstates of the unperturbed Hamiltonian H_0 ($1 = \sum_s |s\rangle\langle s|$) between the two coordinate operators, we obtain

$$\begin{aligned} \langle \Delta x \rangle_r &= \frac{ieE}{2\hbar} \sum_s \int_0^t d\tau \left(\langle r | e^{iH_0\tau/\hbar} x e^{-iH_0\tau/\hbar} | s \rangle \langle s | e^{iH_0t/\hbar} x e^{-iH_0t/\hbar} | r \rangle \right. \\ &\quad \left. - \langle r | e^{iH_0t/\hbar} x e^{-iH_0t/\hbar} | s \rangle \langle s | e^{iH_0\tau/\hbar} x e^{-iH_0\tau/\hbar} | r \rangle \right) e^{i\omega\tau} \\ &\quad + (\omega \rightarrow -\omega) \\ &= \frac{ieE}{2\hbar} \sum_s \int_0^t d\tau \left(e^{i(E_r - E_s + \hbar\omega)\tau/\hbar} e^{i(E_s - E_r)t/\hbar} \right. \\ &\quad \left. - e^{i(E_r - E_s)t/\hbar} e^{i(E_s - E_r + \hbar\omega)\tau/\hbar} \right) \langle r | x | s \rangle \langle s | x | r \rangle \\ &\quad + (\omega \rightarrow -\omega). \end{aligned} \quad (122)$$

We introduce the notation $X_{rs} \equiv \langle r | x | s \rangle$ for the matrix elements of the coordinate operator. Note that these matrix elements in eq. (122) are accompanied by time-development phases $e^{i(E_r - E_s)t/\hbar}$ of *purely harmonic form*: they are the precise correlates in modern quantum mechanics of the substitute oscillators of Ladenburg and Reiche (1923) or, equivalently, the virtual oscillators of BKS, as was clearly realized, for instance, by Landé (1926) (cf. the discussion at the end of sec. 4.3).²⁰⁵

Performing the time integral in eq. (122), we find

$$\begin{aligned} \langle \Delta x \rangle_r &= \frac{eE}{2} \sum_s \left[\frac{e^{i(E_r - E_s + \hbar\omega)t/\hbar} - 1}{E_r - E_s + \hbar\omega} e^{i(E_s - E_r)t/\hbar} \right. \\ &\quad \left. - \frac{e^{i(E_s - E_r + \hbar\omega)t/\hbar} - 1}{E_s - E_r + \hbar\omega} e^{i(E_r - E_s)t/\hbar} \right] X_{rs} X_{sr} \\ &\quad + (\omega \rightarrow -\omega). \end{aligned} \quad (123)$$

(cf. eqs. (42) and (44) in sec. 6.1 and eqs. (94) and (98) in sec. 5.2). The

²⁰⁵Once the electromagnetic field itself is quantized, it becomes more natural to identify the virtual oscillators of BKS with the Fourier components of the quantized electromagnetic field, which correspond to time-dependent operators creating (or destroying) the photons emitted (or absorbed) by the atom.

coherent terms in $\langle \Delta x \rangle_r$, i.e. the terms with a time-dependence $e^{\pm i\omega t}$ (cf. eq. (46) in sec. 6.1 and eq. (101) in sec. 5.2), are:

$$\langle \Delta x_{\text{coh}} \rangle_r = \frac{eE}{2} \sum_s X_{rs} X_{sr} e^{i\omega t} \left[\frac{1}{E_r - E_s + \hbar\omega} - \frac{1}{E_s - E_r + \hbar\omega} \right] + (\omega \rightarrow -\omega). \quad (124)$$

Using the Bohr frequency condition $\hbar\omega_{rs} = E_r - E_s$, we can write the expression in square brackets in eq. (124) as:

$$\frac{1}{\hbar\omega_{rs} + \hbar\omega} - \frac{1}{\hbar\omega_{sr} + \hbar\omega} = \frac{2\omega_{rs}}{\hbar(\omega_{rs}^2 - \omega^2)}. \quad (125)$$

Inserting this result into eq. (124) and noting that the terms proportional to $\sin \omega t$ vanish, we find the following result for the dipole moment of the system in state r (cf. eq. (6) or eq. (53))

$$P_r(t) = -e \langle \Delta x_{\text{coh}} \rangle_r = \frac{2e^2 E}{\hbar} \sum_s \frac{\omega_{sr} X_{rs} X_{sr}}{\omega_{sr}^2 - \omega^2} \cos \omega t. \quad (126)$$

The sum over s can naturally be separated into states s of higher energy than r , with $\omega_{sr} > 0$, and states t of lower energy, with $\omega_{rt} > 0$ ($\omega_{rt} = 0$ for $r = t$):

$$P_r = \frac{2e^2 E}{\hbar} \left(\sum_s \frac{\omega_{sr} X_{sr} X_{rs}}{\omega_{sr}^2 - \omega^2} - \sum_t \frac{\omega_{rt} X_{rt} X_{tr}}{\omega_{rt}^2 - \omega^2} \right) \cos \omega t. \quad (127)$$

If we recall the correspondence principle for emission (82), and identify D_s^2 with $3(X_\tau^s)^2 = 12A_\tau A_{-\tau}$ and the Fourier coefficients $A_\tau \rightarrow X_{sr}$, $A_{-\tau} \rightarrow X_{rs}$ we get

$$A_{s \rightarrow r} = \frac{64\pi^4 e^2}{hc^3} \nu_{sr}^3 X_{sr} X_{rs}, \quad (128)$$

whence we recover the original form (64) of the dispersion formula

$$P_r = \frac{c^3}{32\pi^4} E \cos \omega t \left(\sum_s \frac{A_{s \rightarrow r}}{\nu_{sr}^2 (\nu_{sr}^2 - \nu^2)} - \sum_t \frac{A_{r \rightarrow t}}{\nu_{rt}^2 (\nu_{rt}^2 - \nu^2)} \right). \quad (129)$$

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.

Returning for a moment to eq. (127), we see that in the Thomson limit where the frequency of incident radiation far exceeds the difference frequencies ω_{rs} for the electron states r, s ,²⁰⁶ the polarization P_r becomes asymptotically

$$P_r \simeq -\frac{2e^2 E}{\hbar\omega^2} \left(\sum_s \omega_{sr} X_{sr} X_{rs} - \sum_t \omega_{rt} X_{rt} X_{tr} \right) \cos \omega t. \quad (130)$$

The preceding equation is in content identical with the next to last (unnumbered) equation in sec. 2 in (Heisenberg, 1925), where the Kramers dispersion theory is explicitly invoked. For large frequencies, we expect the polarization to approach our previously derived result (see eq. (6) or eq. (53)) for the polarization of a charged harmonic oscillator in the limit where $\nu \gg \nu_0$:²⁰⁷

$$P_r = -\frac{e^2 E}{m\omega^2} \cos \omega t, \quad (131)$$

Comparing eq. (130) with eq. (131) we find eq. (16) in (Heisenberg, 1925):

$$h = 4\pi m \left(\sum_s \omega_{sr} X_{sr} X_{rs} - \sum_t \omega_{rt} X_{rt} X_{tr} \right). \quad (132)$$

This result is first obtained by Heisenberg from the Bohr-Sommerfeld quantization condition by applying the quantum-theoretical transcription procedure, which was introduced in sec. 1 of the *Umdeutung* paper and had been inspired by dispersion theory. It replaces the Bohr-Sommerfeld condition as the fundamental quantization constraint in Heisenberg's new theory. That the same result can be obtained directly from the high-frequency limit of the Kramers dispersion formula is clearly regarded by Heisenberg as strong evidence for the validity of his transcription procedure. Using eq. (132), together with the formal transcription of the classical equation of motion, $\ddot{x} + f(x) = 0$ (eq. (11) of the *Umdeutung* paper), Heisenberg (1925) asserts the possibility of "a complete determination not only of frequencies and energy values, but also of quantum-theoretical transition probabilities" (p. 268). As Heisenberg points out, eq. (132) is completely equivalent to the sum rules for oscillator strengths given by Thomas (1925) and Kuhn (1925).²⁰⁸

²⁰⁶Or, alternatively, when the incident photon energy far exceeds the energy needed to ionize the electron, so that the latter can be regarded as essentially a free, unbound particle.

²⁰⁷This result is obtained in (Kuhn, 1925) by equating the energy scattered by an electron in the Thomson limit to the radiation emitted by an oscillating dipole according to the Larmor formula.

²⁰⁸Heisenberg's logic is slightly different from ours. Instead of pointing out that the high-frequency limit (130) of the Kramers dispersion formula and the well-

The realization that eq. (132) is equivalent to (the diagonal matrix elements of) the fundamental commutator relation $[P, X] = \hbar/i$ of modern quantum theory came shortly after this, in the work of Born and Jordan (1925). The recognition of eq. (132) as a commutator is mathematically obscured by the separation of the sum into states higher (s) and lower (t) than the given state r —a separation which is very natural given the history of the Kramers dispersion formula. If Heisenberg had applied his own transcription rules for associating classical variables with quantum two-index quantities to the momentum $P \equiv m\dot{X}$ in the unnumbered equation immediately following (13) in the *Umdeutung* paper (Heisenberg, 1925, p. 267), he would have found (using modern matrix notation):²⁰⁹

$$P_{rs} = im\omega_{rs}X_{rs}. \quad (133)$$

That Heisenberg did not write down this equation is probably, as we suggested above, because he was thinking in terms of the Lagrange rather than the Hamilton formalism. Rewriting eq. (132) as a *single* sum over all states s , but splitting the sum into two equal pieces via the identity $2\omega_{sr} = \omega_{sr} - \omega_{rs}$, we find

$$\begin{aligned} h &= 4\pi m \sum_s \omega_{sr} X_{rs} X_{sr} \\ &= 2\pi m \sum_s (X_{rs} \omega_{sr} X_{sr} - \omega_{rs} X_{rs} X_{sr}) \\ &= -2\pi i \sum_s (X_{rs} P_{sr} - P_{rs} X_{sr}), \end{aligned} \quad (134)$$

where in the last step we used eq. (133). In modern notation, this last expression is immediately recognized as the diagonal matrix element of the fundamental commutator $[X, P] = i\hbar$:

$$i \frac{h}{2\pi} = \langle r | XP - PX | r \rangle$$

established classical result (131) imply Heisenberg's quantization condition (132), Heisenberg (1925, pp. 269–270) points out that eqs. (132) and (130) imply eq. (131). This is only a cosmetic difference. The point of the exercise is still to show that the new quantization condition, found through *Umdeutung* of the derivative of the Bohr-Sommerfeld condition, follows from well-established results in Kramers' dispersion theory and classical electrodynamics. We are nonetheless grateful to Christoph Lehner for alerting us to this point.

²⁰⁹Following Heisenberg's procedure in the *Umdeutung* paper for translating classical equations into quantum-mechanical ones, we would translate his classical equation for momentum, $m\dot{x} = m \sum_{\alpha} a_{\alpha}(n) i\alpha\omega_n e^{i\alpha\omega_n t}$, into the following quantum-mechanical equation: $P(n, n + \alpha) = ima(n, n + \alpha)\omega(n, n + \alpha)$. In modern notation, this becomes: $P_{rs} = imX_{rs}\omega_{rs}$ (no summation).

$$= \sum_s (\langle r|X|s\rangle\langle s|P|r\rangle - \langle r|P|s\rangle\langle s|P|r\rangle). \quad (135)$$

Although Heisenberg recognized the significance of the noncommutativity of quantum-theoretic quantities in his formalism (see the last three paragraphs of sec. 1), the simplicity of $x(t)p(t) - p(t)x(t)$ implied by his fundamental quantization relation (132) eluded him. He was thinking in terms of velocity rather than momentum. Moreover, even if he had been thinking in terms of momentum, the origin of his quantization condition in dispersion theory might well have prevented him from rewriting the summations the way we did in eq. (134).

7.2 Spontaneous emission

To begin with, we note that we are dealing throughout with the dipole approximation, which is implicit in the 1924 work, corresponding to the regime where the wavelength of light is much larger than atomic dimensions (or equivalently, where photon momentum is much smaller than electron momentum). Once again, note that the notation of (Van Vleck, 1924b, eq. (1)),

$$\begin{aligned} x &= \sum_{\tau_1\tau_2\tau_3} X(\tau_1, \tau_2, \tau_3) \cos \{2\pi(\tau_1\omega_1 + \tau_2\omega_2 + \tau_3\omega_3)t + \dots\} \\ &= \sum \left\{ \frac{1}{2} X(\tau_1, \tau_2, \tau_3) e^{+2\pi i(\tau_1\omega_1 + \tau_2\omega_2 + \tau_3\omega_3)t + \dots} \right. \\ &\quad \left. + \frac{1}{2} X(\tau_1, \tau_2, \tau_3) e^{-2\pi i(\tau_1\omega_1 + \tau_2\omega_2 + \tau_3\omega_3)t + \dots} \right\}, \end{aligned} \quad (136)$$

implies that van Vleck's $D^2 = X^2 + Y^2 + Z^2$ (Van Vleck, 1924b, line following eq. (8)) corresponds to four times the square of the matrix element of the quantum position operator appearing in the dipole transition formulas of modern quantum mechanics. For the latter we shall follow the treatment of (Baym, 1969, Ch. 13).

In the dipole approximation, the spontaneously emitted power per unit solid angle is given by (Baym, 1969, p. 282, eq. 13–100), for emitted light of polarization vector $\vec{\lambda}$, in a transition from state r to state s :

$$\begin{aligned} \frac{dP}{d\Omega} &= \frac{\omega^4 e^2}{2\pi c^3} \langle r|\vec{\lambda} \cdot \vec{x}|s\rangle\langle s|\vec{\lambda} \cdot \vec{x}|r\rangle \\ &= \sum_{i,j=1}^3 \frac{\omega^4 e^2}{2\pi c^3} \lambda_i \lambda_j \langle r|x_i|s\rangle\langle s|x_j|r\rangle. \end{aligned} \quad (137)$$

Here (unlike Baym) we take real polarization vectors $\vec{\lambda}$ (plane polarized) rather

than complex (circularly polarized) ones as our basis. We want the total spontaneously emitted power in any event, summed over the two possible polarizations for any momentum vector \vec{k} of the emitted photon (so the basis of photon states is irrelevant). This requires the polarization sum

$$\sum_{\lambda=1}^2 \lambda_i \lambda_j = \delta_{ij} - \hat{k}_i \hat{k}_j, \quad (i, j = 1, 2, 3), \quad (138)$$

which follows from the fact that the two polarization vectors are any pair of orthogonal unit vectors perpendicular to the unit vector \hat{k} along the photon direction. Finally, we want the total power emitted in any direction, so the polarization sum (138) must be integrated over all solid angles:

$$\int d\Omega_{\hat{k}} (\delta_{ij} - \hat{k}_i \hat{k}_j) = 4\pi \left(\frac{2}{3} \delta_{ij} \right). \quad (139)$$

The Einstein coefficient $A_{r \rightarrow s}$ in (Van Vleck, 1924b, eqs. (5) and (9)) refers to a rate of photon emission (not energy emission) so we must divide eq. (137) by $\hbar\omega$. Putting together the above results, we find:

$$A_{r \rightarrow s} = \frac{1}{\hbar\omega} \int d\Omega_{\hat{k}} \frac{dP}{d\Omega_{\hat{k}}} = \frac{\omega^4 e^2}{2\pi \hbar \omega c^3} \frac{8\pi}{3} \sum_i \langle r|x_i|s \rangle \langle s|x_i|r \rangle. \quad (140)$$

Using the notation $X_{rs} \equiv \langle r|x|s \rangle$, etc. for the matrix elements of position introduced above we can rewrite this as:

$$A_{r \rightarrow s} = \frac{\omega^4 e^2}{2\pi \hbar \omega c^3} \frac{8\pi}{3} (|X_{rs}|^2 + |Y_{rs}|^2 + |Z_{rs}|^2). \quad (141)$$

Replacing the matrix elements X_{rs} , Y_{rs} , and Z_{rs} by the amplitude D_r in the correspondence limit as indicated in the preceding section (cf. the remarks preceding eq. (128)) and substituting $\omega = 2\pi\nu$, we arrive at:

$$A_{r \rightarrow s} = \frac{16\pi^4 e^2 \nu^3}{3hc^3} D_r^2. \quad (142)$$

D_r^2 is the amplitude defined by (Van Vleck, 1924b) immediately following eq. (8), to be replaced by $D_r(\tau_1, \tau_2, \tau_3)^2$ in eq. (9), with which eq. (142) is seen to be identical.

7.3 Absorption

The Einstein formula for absorption (Van Vleck, 1924b, eq. (6)), when combined with the stimulated emission (“negative absorption”) term to yield (ibid., eq. 15)), leads directly to the correspondence limit result (ibid., eq. (16)). Here, we check the identity of eq. (15) in (Van Vleck, 1924b) (more precisely, the unnumbered equation immediately following this one) with the modern absorption calculation given in (Baym, 1969). For the rate of absorption of light leading to a transition from state s to (higher) state r , (Baym, 1969, eq. 13–40) reads (in the dipole approximation, $\vec{j}_{\vec{k}} \rightarrow \vec{p}/m$):

$$\Gamma_{s \rightarrow r}^{\text{abs}} = \frac{2\pi e^2}{\hbar^2 c^2} \frac{\omega^2}{(2\pi c)^3} \int d\Omega_{\vec{k}} \sum_{\lambda} \langle s | \vec{\lambda} \cdot \frac{\vec{p}}{m} | r \rangle \langle r | \vec{\lambda} \cdot \frac{\vec{p}}{m} | s \rangle |A_{\vec{k}\lambda}|^2. \quad (143)$$

As usual, in the dipole approximation we can use (Baym, 1969, eq. 13–98) to replace matrix elements of the momentum operator with those of the coordinate operator (using the equations of motion). For Hamiltonians of the form $H = (\vec{p}^2/2m) + V(\vec{x})$,

$$[H, x_j] = \frac{1}{2m} [p_i p_i, x_j] = \frac{1}{m} p_i [p_i, x_j] = \frac{p_i \hbar}{m i} \delta_{ij} = \frac{\hbar p_j}{i m}, \quad (144)$$

whence

$$\begin{aligned} \langle r | \frac{\vec{p}}{m} | s \rangle &= \frac{i}{\hbar} \langle r | [H, \vec{x}] | s \rangle \\ &= \frac{i}{\hbar} (E_r - E_s) \langle r | \vec{x} | s \rangle \\ &= i\omega \langle r | \vec{x} | s \rangle, \end{aligned} \quad (145)$$

where $\hbar\omega = E_r - E_s$. Once again, in eq. (145), we see the “monstrous” difference frequencies characteristic of quantum theory, which wreaked havoc on classical interpretations of radiation phenomena, making their appearance in the modern formalism. Accordingly, eq. (143) becomes

$$\Gamma_{s \rightarrow r}^{\text{abs}} = \frac{2\pi e^2}{\hbar^2 c^2} \frac{\omega^4}{(2\pi c)^3} \int d\Omega_{\vec{k}} \sum_{\lambda} \langle s | \lambda_i x_i | r \rangle \langle r | \lambda_j x_j | s \rangle |A_{\vec{k}\lambda}|^2. \quad (146)$$

Now we are going to assume that the ambient light is unpolarized and isotropic so that the squared amplitude $|A_{\vec{k}\lambda}|^2$ is in fact independent of λ, \hat{k} , and the only angular dependence comes in via the polarization vectors. The angle average of the polarization sum in eq. (146) can then be performed as in eq.

(139) to yield

$$\Gamma_{s \rightarrow r}^{\text{abs}} = \frac{4\pi e^2}{3\hbar^2 c^2} \frac{\omega^4}{(2\pi c)^3} \langle s|x_i|r \rangle \langle r|x_i|s \rangle \int d\Omega_{\hat{k}} |A_{\vec{k}\lambda}|^2. \quad (147)$$

Next, we need to establish the relation between the squared mode amplitudes $|A_{\vec{k}\lambda}|^2$ and the specific energy density function $\rho(\nu)$ defined as the energy per unit volume per unit frequency interval. The mode amplitudes $A_{\vec{k}\lambda}$ correspond to discrete modes for electromagnetic radiation in a box of volume V , with each mode contributing energy density

$$\frac{1}{V} |A_{\vec{k}\lambda}|^2 \frac{\omega}{2\pi c^2} \quad (148)$$

(Baym, 1969, eq. 13–14). As the box volume goes to infinity we have the usual correspondence

$$\frac{1}{V} \sum_{\vec{k}} \rightarrow \int \frac{k^2 dk d\Omega_{\hat{k}}}{(2\pi)^3}, \quad (149)$$

so that the total energy density *between frequency ν and frequency $\nu + \Delta\nu$* is

$$\begin{aligned} \rho(\nu)\Delta\nu &= \frac{1}{V} \sum_{2\pi\nu < kc < 2\pi(\nu+\Delta\nu)} 2|A_{\vec{k}\lambda}|^2 \frac{\omega^2}{2\pi c^2} \\ &\rightarrow \frac{1}{(2\pi)^3} \int d\Omega_{\hat{k}} \int_{2\pi\nu/c}^{2\pi(\nu+\Delta\nu)/c} dk k^2 \frac{\omega^2}{2\pi c^2} 2|A_{\vec{k}\lambda}|^2. \end{aligned} \quad (150)$$

Note that although we continue to write the mode amplitudes $A_{\vec{k}\lambda}$ as depending on polarization and momentum vector of the photon, we are really assuming that there is no dependence on the polarization or photon *direction*. Hence the factor of 2, with no remaining sum over λ . Eq. (150) gives

$$\rho(\nu)\Delta\nu = \frac{1}{(2\pi)^3} \frac{2\pi}{c} k^2 \frac{\omega^2}{2\pi c^2} 2 \int d\Omega_{\hat{k}} |A_{\vec{k}\lambda}|^2 \Delta\nu, \quad (151)$$

or, equivalently

$$\int d\Omega_{\hat{k}} |A_{\vec{k}\lambda}|^2 = \frac{4\pi^3 c^5}{\omega^4} \rho(\nu). \quad (152)$$

Inserting eq. (152) into eq. (147) and multiplying by $\hbar\omega$ to get the rate of energy absorption (instead of the number rate of photon absorption) we find,

using the usual association of squares of matrix elements of the position operator to the classical orbit amplitude $\frac{1}{4}D_r^2$,

$$\begin{aligned}\hbar\omega\Gamma_{s\rightarrow r}^{\text{abs}} &= \frac{4\pi e^2\omega}{3\hbar c^2} \frac{\omega^4}{(2\pi c)^3} \frac{4\pi^3 c^5}{\omega^4} \rho(\nu) \frac{1}{4} D_r^2 \\ &= \frac{2\pi^3 e^2}{3h} \nu \rho(\nu) D_r^2,\end{aligned}\tag{153}$$

which coincides with the first term in van Vleck's equation (Van Vleck, 1924b, the equation following eq. (15)) for the part of the total absorption rate due to upward transitions. Of course, the second (negative absorption, or stimulated emission) term is of exactly the same form (with a minus sign) due to the symmetry of the Einstein B coefficients.

8 Conclusion

Our study of Van Vleck's two-part paper on the application of the correspondence principle to the interaction of matter and radiation (Van Vleck, 1924b,c) has led us to consider three clusters of questions. First, there are questions about the paper itself. What made Van Vleck decide to work in this area? He had not published on radiation theory before. And—as one is inevitably tempted to ask—why did Van Vleck not take the next step and arrive at something like matrix mechanics? That gets us to the second cluster of questions, about the developments in quantum theory that provide the natural context for Van Vleck's work, especially the transition from the old quantum theory of Bohr and Sommerfeld to matrix mechanics. What was important for this development and what was not? The third group of questions concerns the relative importance of American contributions to these developments. In this final section we collect the (partial) answers we have found to these biographical, conceptual, and sociological questions.

Let us first dispose of the issue of American contributions to early quantum theory. Since we focused on the work of only two individuals, Van Vleck and Slater, we are in no position to draw strong conclusions. Still, it seems safe to say that our study supports the thesis of Sam Schweber (1986) and others that, by the early 1920s, the United States had a homegrown tradition in quantum theory, which, to be sure, was reinforced, but certainly not created by the influx of European émigrés in the 1930s. We are less sanguine about the thesis of Alexi Assmus (1992) that American theorists contributed mainly to molecular rather than to atomic physics, although she may be right that Slater and Van Vleck are just exceptions to the rule (see sec. 2.4). However, we did come across several other contributions (some admittedly minor) to

atomic theory by Americans (Breit, Davisson, Hoyt, Kemble) or by Europeans working in America (Epstein, Swann). And we do want to emphasize that the contributions to atomic theory by our main protagonists were absolutely first rate, even if they did not always receive the recognition they deserved from their European colleagues (see the correspondence between Born and Van Vleck cited in secs. 2.4 and 5.2). The quickly refuted but highly influential Bohr-Kramers-Slater (BKS) theory was built around Slater's idea of a virtual radiation field emitted by an atom while in a stationary state (see sec. 4.1). The derivation of a correspondence principle of absorption for a general non-degenerate multiply-periodic system, the centerpiece of (Van Vleck, 1924b,c), is a *tour de force* that may well have been the most sophisticated application of the correspondence principle in the old quantum theory. All in all, the Americans had definitely established a presence in atomic theory by the early 1920s. In the period we examined, they were certainly more prominent than the British, not to mention the French. Ultimately, however, the decisive steps were taken in Europe, not in the United States.

This brings us to the question of why Van Vleck stopped short of these decisive steps. Before we offer our best guess as to why Van Vleck did not do what he did not do, we want to say a few words about why he did what he did. His papers on the correspondence principle for absorption (Van Vleck, 1924a,b,c) constitute his first foray into quantum radiation theory. His earlier publications had dealt with such topics as the extension of Bohr's model of the atom to helium and the specific heat of molecular hydrogen. The formulation of a correspondence principle for absorption, Van Vleck told Kuhn in his interview for the AHQP in 1963, had been triggered by a comment of his Minnesota colleague Breit (see also Van Vleck, 1924a, p. 28). Breit's remark, we conjectured (in sec. 5.3), may have directed Van Vleck to the work of Ladenburg and Reiche (1923), who proposed quantum formulae for emission, absorption, and dispersion, invoking but not always correctly implementing the correspondence principle. Van Vleck likewise proposed quantum formulae for emission and absorption and used his considerable expertise in classical mechanics to show that these formulae as well as the Kramers dispersion formula merged with the classical formulae in the limit of high quantum numbers.

So why did Van Vleck not take the next step? The trivial explanation is that he was too busy working on his *Bulletin* for the *National Research Council* on the old quantum theory (Van Vleck, 1926) to pursue his own research. But even if he had not been burdened by this *Bulletin*, we seriously doubt that Van Vleck would have done what Heisenberg did—as he himself acknowledged both in a biographical statement prepared for the AHQP and in his interview for the project (see sec. 1.1). Van Vleck, it seems, was too wedded to the orbits of the Bohr-Sommerfeld theory to completely discard them, a prerequisite for Heisenberg's *Umdeutung*. This is clear at several points in (Van Vleck, 1924b). At the end of sec. 1, for instance, we find a formula expressing the Einstein

coefficient $A_{r \rightarrow s}$ as an average over the frequencies of orbits, not allowed by the Bohr-Sommerfeld quantization condition, between the initial state r and the final state s . Sec. 2 of the paper is devoted to “a correspondence principle for *orbital distortions*” (Van Vleck, 1924b, p. 334, our emphasis). On the issue of how seriously one should take the orbits of the Bohr-Sommerfeld theory, Van Vleck might have benefited from direct contact with the Europeans. He had the distinct disadvantage of *reading* Sommerfeld instead of *talking* to Bohr and his circle.²¹⁰ Bohr and Pauli certainly prepared Heisenberg for the step of leaving orbits behind.

The emphasis on observable quantities in the *Umdeutung* paper, however, struck a chord with Van Vleck, who had been primed for such a positivist turn by his Harvard teacher Bridgman.²¹¹ Explaining the new quantum mechanics in *Chemical Reviews* in 1929,²¹² he wrote:

Heisenberg’s epoch-making development of the matrix theory was spurred by Born’s repeated emphasis to his colleagues at Göttingen that the reason the old quantum theory was then (1925) failing was that we were all too anxious to use the same concepts of space and time within the atom as in ordinary measurable large-scale events. . . . the concepts of distance and time have a meaning only when we tell how they can be measured. This is very nicely emphasized in Bridgman’s recent book, “The Logic of Modern Physics” [Bridgman, 1927] . . . one cannot use a meter stick to measure the diameter of an atom, or an alarm clock to record when an electron is at the perihelion of its orbit. Consequently we must not be surprised if within the atom the correlation of space and time is something which cannot be visualized, and that models cannot be constructed with the same kind of mechanics as Henry Ford uses in designing an automobile. . . . The goal of theoretical physics and chemistry must ever be to explain observable rather than unobservable phenomena . . . What the physicist observes about an atom is primarily its radiations . . . We may say that we have a sound atomic

²¹⁰According to Alexi Assmus (1992, pp. 8, 15), Americans had a tendency to follow Sommerfeld rather than Bohr anyway.

²¹¹In the biographical note written for the AHQP, Van Vleck wrote: “I suspect that Bridgman’s operational philosophy may have subconsciously influenced my approach to theoretical physics.” At a ceremony honoring Bridgman’s 1946 Nobel prize, Slater went as far as suggesting a genetic link between Bridgman’s operationalism and Heisenberg’s uncertainty principle! Schweber (1990) quotes Slater as saying on this occasion: “It is very likely that this principle, so much like Bridgman’s attitude, is actually derived to a very considerable extent from Bridgman’s thinking” (p. 391).

²¹²For the benefit of the chemists, Van Vleck (1929) compared a matrix to a baseball schedule: “the entry in row 3 and column 2, for instance, gives information about a transition between a 3 and 2 quantum state, just as the analogous baseball entry does about the meetings between teams 3 and 2” (p. 469).

theory when we have a set of a small number of mathematical postulates from which these observed things can be calculated correctly, even though it forces us to discard the usual space-time models (Van Vleck, 1929, p. 468).

Van Vleck was thus ready enough to give up orbits once Heisenberg had shown the way. He failed to take this step on his own.

The study of Van Vleck's paper illuminates various aspects of the transition from the old quantum theory to matrix mechanics that tend to get obscured when one approaches these developments through, say, (Kramers and Heisenberg, 1925). Most importantly perhaps, following (Van Vleck, 1924b,c) rather than (Kramers and Heisenberg, 1925) or (Born, 1924), we were able to give a transparent and explicit version of the derivation needed to show that the crucial Kramers dispersion formula reduces to the classical formula in the limit of high quantum numbers (see secs. 5.1–5.2 for the special case of a simple harmonic oscillator, sec. 6.2 for the generalization to arbitrary non-degenerate multiply-periodic systems, and sec. 7.1 for a closely analogous derivation of the Kramers formula in modern quantum mechanics). That Van Vleck confirmed the Kramers dispersion formula without relying on the Bohr-Kramers-Slater (BKS) theory makes it particularly clear that matrix mechanics grew directly out of dispersion theory and that BKS was mainly a sideshow (see sec. 4). The only element of the BKS theory used by Van Vleck is the concept of virtual oscillators. We saw that this concept actually predates BKS. 'Virtual oscillators' was Bohr's new name for the substitute oscillators introduced into dispersion theory the year before and at Bohr's suggestion by Ladenburg and Reiche (1923). In addition to popularizing the notion of virtual oscillators, BKS may have contributed to instilling skepticism about the electron orbits of the Bohr-Sommerfeld theory. In that sense, it might have helped Van Vleck had he embraced BKS more wholeheartedly. Overall, however, we argued that BKS played only a very limited role in the breakthrough to matrix mechanics. The broad acceptance of Einstein's light-quantum concept following the discovery of the Compton effect played no role in this development. Physicists working in dispersion theory, while accepting the Compton effect as decisive evidence for light quanta, happily continued to treat light as a wave phenomenon.

What was it about dispersion theory that made it so important for the transition from the Bohr-Sommerfeld theory to the theory of Heisenberg's *Umdeutung* paper? As we suggested in the introduction of sec. 3, the answer is that the discrepancy between orbital frequencies and radiation frequencies—one of the most radical, if not *the* most radical aspect of the Bohr model of the atom—manifested itself glaringly and unavoidably in dispersion theory. The natural approach to adapting the successful classical dispersion theory of Helmholtz, Lorentz and Drude to Bohr's new theory inevitably led to a dispersion formula with resonance poles at the orbital frequencies (Sommerfeld, 1915b; Debye,

1915; Davisson, 1916; Epstein, 1922c), whereas experiment clearly indicated that the resonance poles should be at the radiation frequencies, associated in Bohr’s theory with transitions between orbits. Employing Einstein’s A and B coefficients and Bohr’s correspondence principle (in conjunction with techniques from celestial mechanics customized to the problems at hand) and building on pioneering work by Ladenburg (1921) and Ladenburg and Reiche (1923), Kramers (1924a,b) constructed a quantum formula for dispersion with resonance poles at the transition frequencies rather than at the orbital frequencies and claimed that this formula merged with the classical formula in the limit of high quantum numbers. Van Vleck (1924b,c) and Born (1924) were the first to publish an explicit proof that the Kramers quantum formula does indeed merge with the classical formula for dispersion in a general non-degenerate multiply-periodic system in the correspondence limit. The three key moves in translating the classical formula into a quantum-theoretical one were to (1) replace orbital frequencies by transition frequencies; (2) relate amplitudes to Einstein’s A coefficients; and (3) replace derivatives with respect to the action variable by difference quotients. The first move goes back to the embryonic version of the correspondence principle in (Bohr, 1913) (Heilbron and Kuhn, 1969, pp. 274–275). Ladenburg (1921) introduced the second move. It was made more precise by Kramers and Van Vleck (cf. Jordan’s remarks quoted in sec. 2.4). Born (1924) is usually credited with the third move and the rule for replacing derivatives by difference quotients is sometimes even called “Born’s correspondence rule” (Jammer, 1966, p. 193) or “Born’s discretizing rule” (Cassidy, 1991, p. 181). It was found independently, however, by both Kramers and Van Vleck (see the discussion at the end of sec. 5.2).

The Kramers dispersion formula no longer contains any reference to the orbits of the Bohr-Sommerfeld theory, but only to transitions between them. This signaled to Heisenberg that orbits could be dispensed with altogether. Dispersion theory further told Heisenberg how to generate quantum formulae from classical formulae in his *Umdeutung* scheme. The procedure consisted of the same three moves listed above: one had to replace (1) classical frequencies (more specifically: the Fourier overtones of the classical mechanical motion) by quantum transition frequencies; (2) classical amplitudes associated with definite orbits by quantum transition amplitudes associated with pairs of stationary states; and (3) derivatives by difference quotients.²¹³ Dispersion theory also furnished the fundamental quantization condition for Heisenberg’s new theory. Heisenberg formulated this condition by applying his *Umdeutung* procedure to the Bohr-Sommerfeld quantum condition, which was no longer acceptable because of its explicit reference to orbits. That Heisenberg’s new

²¹³Another factor in Van Vleck’s failure to take the next step might have been that he used these correspondence-principle replacements to check rather than to construct quantum formulae. However, even though Born had emphasized the constructive use of these replacements (see sec. 5.2), he did not do what Heisenberg did either.

condition also emerged in the high-frequency limit of the Kramers dispersion formula (see sec. 7.1) convinced him that he had found a sensible replacement for the Bohr-Sommerfeld condition. The relevant formula had been found in quantum dispersion theory before and was known as the Thomas-Kuhn(-Reiche) sum rule (Thomas, 1925; Kuhn, 1925; Reiche and Thomas, 1925). Van Vleck actually had been the first to find this rule, even though he did not emphasize the result because he thought it was problematic (see sec. 3.5). In his later years, Van Vleck nonetheless used to mention this achievement with pride to several of his colleagues (Roger Stuewer, private communication). The Kramers dispersion formula and the Thomas-Kuhn sum rule are the critical physical ingredients in the first two sections of (Heisenberg, 1925), in which the *Umdeutung* procedure is motivated. Van Vleck was fully cognizant of these same ingredients by mid-1924. Van Vleck can thus truly be said to have been on the verge of *Umdeutung* in Minnesota in the summer of 1924.

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