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Joint ICTP-TWAS School on Coherent State Transforms, Time-Frequency and Time-Scale Analysis, Applications

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Coherent states, POVM, quantization and measurement contd.

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Contents

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1. Weyl-Heisenberg covariant integral quantization(s)

Weyl-Heisenberg group and algebra, Fock or number representation

- Weyl-Heisenberg group $G_{\mathrm{WH}} = \{(s,z)\,,\ s\in\mathbb{R}\,,\ z\in\mathbb{C}\}$ with multiplication law
$$(s,z)(s',z') = (s+s'+\mathrm{Im}(z\bar{z}'), z+z')$$
- Let $\mathcal{H}$ be a separable (complex) Hilbert space with orthonormal basis $e_0, e_1, \ldots, e_n \equiv |e_n\rangle, \ldots,$ (e.g. the Fock space with $|e_n\rangle \equiv |n\rangle$).
- Lowering and raising operators a and $a^\dagger$:
$$\begin{aligned} a\,|e_n\rangle &= \sqrt{n}|e_{n-1}\rangle\,, \quad a|e_0\rangle = 0\,, \\ a^\dagger\,|e_n\rangle &= \sqrt{n+1}|e_{n+1}\rangle\,. \end{aligned}$$
- Operator algebra $\{a, a^\dagger, 1\}$ obeys the ccr
$$[a, a^\dagger] = 1\,,$$
and represents the Lie Weyl-Heisenberg algebra
- Number operator: $N = a^\dagger a$, spectrum $\mathbb{N}$, $N|e_n\rangle = n|e_n\rangle$.

Unitary Weyl-Heisenberg group representation and standard CS

- Consider the center $C = \{(s,0)\,,\ s \in \mathbb{R}\}$ of G_{WH}. Then, set X is the coset $X = G_{\mathrm{WH}}/C \sim \mathbb{C}$ with measure $\mathrm{d}^2 z/\pi$.
- To each $z \in \mathbb{C}$ corresponds the (unitary) displacement ($\sim$ Weyl) operator $D(z)$:

$$\mathbb{C} \ni z \mapsto D(z) = e^{za^\dagger - \bar{z}a}\,.$$

- Space inversion → Unitarity:

$$D(-z) = (D(z))^{-1} = D(z)^\dagger\,.$$

- Addition formula (Quantum Mechanics in a nutshell!):

$$D(z)D(z') = e^{\frac{1}{2}(z\bar{z'} - \bar{z}z')}D(z+z') = e^{(z\bar{z'} - \bar{z}z')}D(z')D(z)\,,$$

  i.e. $z \mapsto D(z)$ is a projective representation of the abelian group $\mathbb{C}$.

- Standard (i.e., Schrödinger-Klauder-Glauber-Sudarshan) CS

$$|z\rangle = D(z)|e_0\rangle\,,$$

Quantization(s) with weight function(s) I

- Let $\varpi(z)$ be a function on the complex plane obeying $\varpi(0) = 1$. Suppose that it allows to define a bounded operator M on $\mathfrak{H}$ through the operator-valued integral
$$\mathsf{M} = \int_{\mathbb{C}} \varpi(z) D(z) \, \frac{\mathrm{d}^2 z}{\pi} \, .$$
- Then, the family of displaced $\mathsf{M}(z) := D(z)\mathsf{M}D(z)^\dagger$ under the unitary action $D(z)$ resolves the identity
$$\int_{\mathbb{C}} \mathsf{M}(z) \, \frac{\mathrm{d}^2 z}{\pi} = I \, .$$
- It is a direct consequence of $D(z)D(z')D(z)^\dagger = e^{z\bar{z}' - \bar{z}z'} D(z')$, of $\int_{\mathbb{C}} e^{z\bar{\xi} - \bar{z}\xi} \, \frac{\mathrm{d}^2\xi}{\pi} = \pi\delta^2(z)$, and of $\varpi(0) = 1$ with $D(0) = I$.

Quantization(s) with weight function(s) II

- The resulting quantization map is given by

$$f \mapsto A_f = \int_{\mathbb{C}} \mathsf{M}(z)\, f(z)\, \frac{\mathrm{d}^2 z}{\pi}\,.$$

- Equivalently $A_f = \int_{\mathbb{C}} \varpi(z)\, D(z)\, \hat{f}(-z)\, \frac{\mathrm{d}^2 z}{\pi}$, where is involved the symplectic Fourier transform $\hat{f}(z) = \int_{\mathbb{C}} e^{z\bar{\xi} - \bar{z}\xi} f(\xi)\, \frac{\mathrm{d}^2 \xi}{\pi}$
- Covariance:

$$A_{f(z-z_0)} = D(z_0) A_{f(z)} D(z_0)^{\dagger}\,.$$

- Properties:

$$\begin{aligned} A_{f(-z)} = \mathsf{P} A_{f(z)} \mathsf{P}, \forall\, f \quad &\Longleftrightarrow \quad \varpi(z) = \varpi(-z), \,\forall\, z\,, \\ A_{\overline{f(z)}} = A^{\dagger}_{f(z)}, \forall\, f \quad &\Longleftrightarrow \quad \overline{\varpi(-z)} = \varpi(z), \,\forall\, z\,, \end{aligned}$$

where $\mathsf{P} = \sum_{n=0}^{\infty} (-1)^n |e_n\rangle\langle e_n|$ is the parity operator.

Rotational covariance!

- Define the unitary representation $\theta \mapsto U_{\mathbb{T}}(\theta)$ of the torus $\mathbb{S}^1$ on the Hilbert space $\mathcal{H}$ as the diagonal operator

  $$U_{\mathbb{T}}(\theta)|e_n\rangle = e^{i(n+\nu)\theta}|e_n\rangle \ ,$$

  where ν is arbitrary real.

- From the matrix elements of $D(z)$ one proves easily the rotational covariance property

  $$U_{\mathbb{T}}(\theta)D(z)U_{\mathbb{T}}(\theta)^{\dagger} = D\left(e^{i\theta}z\right) \ ,$$

- and its immediate consequence on the nature of M and the covariance of A_f,

  $$\begin{aligned} U_{\mathbb{T}}(\theta)A_f U_{\mathbb{T}}(-\theta) = A_{T(\theta)f} \quad &\Longleftrightarrow \quad \varpi\left(e^{i\theta}z\right) = \varpi(z)\,,\ \forall\, z\,,\theta \\ &\Longleftrightarrow \quad \mathsf{M}\ \text{diagonal}\,, \end{aligned}$$

  where $T(\theta)f(z) := f\left(e^{-i\theta}z\right)$.

CCR is (almost always) the rule!

- The quantization map $f \mapsto A_f$ yields the canonical commutation rule

  $$[a, a^\dagger] = I$$

  for all even real weight function ϖ.

- Indeed

  $$A_z = a \, , \quad A_{\overline{f(z)}} = A^\dagger_{f(z)} \, .$$

- Equivalently, with $z = (q + ip)/\sqrt{2}$,

  $$A_q = \frac{a + a^\dagger}{\sqrt{2}} := Q \, , \; A_p = \frac{a - a^\dagger}{i\sqrt{2}} := P \, , \; [Q, P] = iI$$

- Moreover, if $|\varpi(z)| = 1$

  $$\mathrm{tr}(A^\dagger_f A_f) = \int_{\mathbb{C}} |f(z)|^2 \frac{\mathrm{d}^2 z}{\pi} \, ,$$

  which means that the map $f \mapsto A_f$ is invertible through a trace formula.

Wigner-Weyl, CS, normal, and other, quantizations

- The normal, Wigner-Weyl and anti-normal (i.e., anti-Wick or Berezin or CS) quantizations correspond to $s \to 1_-$, $s = 0$, $s = -1$ resp. in the specific choice [a]

$$\varpi_s(z) = e^{s|z|^2/2}\,, \quad \mathrm{Re}\, s < 1.$$

- This yields a diagonal $\mathsf{M} \equiv \mathsf{M}_s$ with

$$\langle e_n | \mathsf{M}_s | e_n \rangle = \frac{2}{1-s} \left(\frac{s+1}{s-1} \right)^n \,,$$

and so

$$\mathsf{M}_s = \int_{\mathbb{C}} \varpi_s(z) D(z) \, \frac{\mathrm{d}^2 z}{\pi} = \frac{2}{1-s} \exp \left[\ln \left(\frac{s+1}{s-1} \right) a^{\dagger} a \right] \,.$$

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[a] K.E. Cahill and R. Glauber, Ordered expansion in Boson Amplitude Operators, *Phys. Rev.* **117** 1857-1881 (1969)

Wigner-Weyl, CS, normal, and other, quantizations II

- The case $s = -1$ corresponds to the CS (anti-normal) quantization, since

$$\mathsf{M} = \lim_{s \to -1} \frac{2}{1-s} \exp\left(\ln \frac{s+1}{s-1} a^\dagger a \right) = |e_0\rangle\langle e_0| \,,$$

  and so

$$A_f = \int_{\mathbb{C}} D(z) \mathsf{M} D(z)^\dagger \, f(z) \, \frac{\mathrm{d}^2 z}{\pi} = \int_{\mathbb{C}} |z\rangle\langle z| \, f(z) \, \frac{\mathrm{d}^2 z}{\pi} \,.$$

- The choice $s = 0$ implies $\mathsf{M} = 2\mathsf{P}$ and corresponds to the Wigner-Weyl quantization. Then

$$A_f = \int_{\mathbb{C}} D(z) \, 2\mathsf{P} \, D(z)^\dagger \, f(z) \, \frac{\mathrm{d}^2 z}{\pi} \,.$$

- The case $s = 1$ is the normal quantization in an asymptotic sense.

- The parameter s was originally introduced by Cahill and Glauber in view of discussing the problem of expanding an arbitrary operator as an ordered power series in a and $a^\dagger$, a typical question encountered in quantum field theory, specially in quantum optics. Actually, they were not interested in the question of quantization itself.

Canonical quantization with POVM or not

- Operator M_s is positive unit trace class for $s \leqslant -1$ (and only trace class if $\mathrm{Re}\ s < 0$), i.e., is density operator: quantization has a consistent probabilistic content, the operator-valued measure
$$\mathbb{C} \supset \Delta \mapsto \int_{\Delta \in \mathcal{B}(\mathbb{C})} D(z)\mathsf{M}_s D(z)^\dagger \, \frac{\mathrm{d}^2 z}{\pi}\,,$$
is a <u>positive</u> operator-valued measure.

- Given an elementary quantum energy, say $\hbar\omega$ and with the temperature T-dependent $s = -\coth \dfrac{\hbar\omega}{2k_B T}$ the density operator quantization is Boltzmann-Planck
$$\rho_s = \left(1 - e^{-\frac{\hbar\omega}{k_B T}}\right) \sum_{n=0}^{\infty} e^{-\frac{n\hbar\omega}{k_B T}} |e_n\rangle\langle e_n|\,.$$

- Interestingly, the temperature-dependent operators $\rho_s(z) = D(z)\,\rho_s\,D(z)^\dagger$ defines a Weyl-Heisenberg covariant family of POVM's on the phase space $\mathbb{C}$, the null temperature limit case being the POVM built from standard CS. Physical meaning of this temperature? Noise temperature like in electronics?

Variations on the Wigner function

- The Wigner function is (up to a constant factor) the Weyl transform of the quantum-mechanical density operator. For a particle in one dimension it takes the form (in units $\hbar = 1$)

$$\mathfrak{W}(q,p) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \left\langle q - \frac{y}{2} \right| \rho \left| q + \frac{y}{2} \right\rangle e^{ipy} \, \mathrm{d}y \, . \tag{1}$$

- Adapting this definition to the present context, and given an operator A, the corresponding Wigner function is defined as

$$\mathfrak{W}_A(z) = \mathrm{tr}\left(D(z) 2\mathsf{P} D(z)^{\dagger} A \right) \, , \tag{2}$$

  In the case of the quantization map $f \mapsto A_f$ based on a weight function ϖ, we have

$$\mathfrak{W}_{A_f}(z) = \int_{\mathbb{C}} \widehat{\varpi}(\xi - z) \, f(\xi) \, \frac{\mathrm{d}^2\xi}{\pi} \, , \tag{3}$$

- This becomes in the case of Weyl-Wigner quantization

$$\mathfrak{W}_{A_f} = f \tag{4}$$

  (this one-to-one correspondence of the Weyl quantization is related to the isometry property).

Variations on the Wigner function (continued)

- In the case of the anti-normal quantization, the above convolution corresponds to the Husimi transform (when f is the Wigner transform of a quantum pure state).
- If the quantization map $f \mapsto A_f$ is regular and isometric, the corresponding inverse map $A \mapsto \mathfrak{W}_A$ is given by

$$\mathfrak{W}_A = \mathrm{tr}\left(D(z)\mathsf{M}D(z)^\dagger A\right)\ , \text{ where } \mathsf{M} = \mathsf{M}^\dagger = \int_{\mathbb{C}} \varpi(z) D(z)\, \frac{\mathrm{d}^2 z}{\pi}\,. \tag{5}$$

- In general this map $A \mapsto \mathfrak{W}_A$ is only the dual of the quantization map $f \mapsto A_f$ in the sense that

$$\int_{\mathbb{C}} \mathfrak{W}_A(z) f(z) \frac{\mathrm{d}^2 z}{\pi} = \mathrm{tr}(A\, A_f)\,. \tag{6}$$

- This dual map becomes the inverse of the quantization map only in the case of a Hilbertian isometry.

Quantum harmonic oscillator according to ϖ

- For real even ϖ,

$$A_{q^2} = Q^2 - \partial_z\partial_{\bar z}\varpi|_{z=0} + \frac{1}{2}\left(\partial_z^2\varpi\big|_{z=0} + \partial_{\bar z}^2\varpi\big|_{z=0}\right)$$
$$A_{p^2} = P^2 - \partial_z\partial_{\bar z}\varpi|_{z=0} - \frac{1}{2}\left(\partial_z^2\varpi\big|_{z=0} + \partial_{\bar z}^2\varpi\big|_{z=0}\right)$$

  and so

$$A_{|z|^2} \equiv A_J = a^\dagger a + \frac{1}{2} - \partial_z\partial_{\bar z}\varpi|_{z=0} \, .$$

  where $|z|^2 (= J)$ is the energy (or action variable) for the H.O.

- The difference between the ground state energy $E_0 = 1/2 - \partial_z\partial_{\bar z}\varpi|_{z=0}$, and the minimum of the quantum potential energy $E_m = [\min(A_{q^2}) + \min(A_{p^2})]/2 = -\,\partial_z\partial_{\bar z}\varpi|_{z=0}$ is independent of the particular (regular) quantization chosen, namely $E_0 - E_m = 1/2$ (experimentally verified in 1925).

- In the exponential Cahill-Glauber case $\varpi_s(z) = e^{s|z|^2/2}$ the above operators reduce to

$$A_{|z|^2} = a^\dagger a + \frac{1-s}{2} \, , A_{q^2} = Q^2 - \frac{s}{2} \, A_{p^2} = P^2 - \frac{s}{2} \, .$$

- It has been proven [a] that these constant shifts in energy are inaccessible to measurement: see next section for a detailed analysis in the $s = -1$ (i.e. CS) case.

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[a] H. Bergeron, J.P. G., A. Youssef, Are the Weyl and coherent state descriptions physically equivalent?, Physics Letters A 377 (2013) 598605

Are the canonical and CS quantization physically equivalent?

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[1] H. Bergeron, J.P. G., A. Youssef, Are the Weyl and coherent state descriptions physically equivalent?, *Physics Letters A* **377** (2013) 598605

Quantum harmonic oscillator energy

- CS quantization of the classical harmonic oscillator Hamiltonian $H = \frac{1}{2}(p^2 + q^2) = |z|^2$ gives

$$A_H = A_{|z|^2} = \hat{N} + \mathbb{I}_{\mathcal{H}}\,.$$

- **Time evolution in the phase space:** there is a perfect Gaussian localization in the (q,p) phase space of the corresponding time-evolving probability density, i.e. of the Gaussian $e^{-|z-e^{-i\omega t}z_0|^2}$.

- CS quantization does not fit exactly with the “canonical” one, which consists in just replacing q by Q and p by P in the expressions of the observables $f(q,p)$ and next proceeding with a symmetrization in order to comply with self-adjointness. This ansatz leads to the quantum Hamiltonian $\hat{H} = \frac{1}{2}(P^2 + Q^2) = \hat{N} + (1/2)\,\mathbb{I}_{\mathcal{H}}$.

- Thus there is a shift by $1/2$ between the spectrum of $\hat{H}$ and the CS quantized Hamiltonian A_H. Actually, no physical experiment can discriminate between those two spectra that differ from each other by a simple shift.

The reasoning

- CS quantization of the classical position q provides the usual position operator Q: $A_q = Q$. The latter is self-adjoint and acts as the multiplication operator $Q\psi(x) = x\psi(x)$.
- Operator $Q = \frac{1}{\sqrt{2}}(a + a^\dagger)$ is expressed in basis $|e_n\rangle$ as follows:

$$Q = \frac{1}{\sqrt{2}} \sum_{n=0}^{\infty} \sqrt{n+1}\,(|e_n\rangle\langle e_{n+1}| + |e_{n+1}\rangle\langle e_n|) \tag{7}$$

- Now compare $Q^2 = (A_q)^2$ with A_{q^2}, the CS quantized of the square of the classical position. Simple calculation yields:

$$\begin{aligned} A_{q^2} &= \mathbb{I} + \hat{N} + \frac{1}{2}\sum_{n=0}^{\infty} \sqrt{(n+1)(n+2)}\,(|e_n\rangle\langle e_{n+2}| + |e_{n+2}\rangle\langle e_n|) \\ &= Q^2 + \frac{1}{2}\mathbb{I}\,. \end{aligned} \tag{8}$$

The reasoning continued

- A similar relation holds between the operator P^2 and the CS quantized of p^2:

$$A_{p^2} = \mathbb{I} + \hat{N} - \frac{1}{2}\sum_{n=0}^{\infty}\sqrt{(n+1)(n+2)}\,(|e_n\rangle\langle e_{n+2}| + |e_{n+2}\rangle\langle e_n|)$$
$$= P^2 + \frac{1}{2}\mathbb{I}\,. \qquad (9)$$

- Therefore, **there is a shift by** $\frac{1}{2}\mathbb{I}$ between the operators Q^2 and A_{q^2} resp.(P^2 and A_{p^2}), and, consequently, between their respective spectra. Since the spectrum of Q^2 (resp. P^2) is $\mathbb{R}^+$ with infimum 0, the infimum of the spectrum of A_{q^2} (resp. A_{p^2}) **is** $\frac{1}{2}$.

- In consequence, the difference between the ground state harmonic vibration energy and the zero-point energy ***defined as the minimum of the quantum potential energy*** is still $\frac{1}{2}$ (in suitable units), regardless of the choice between canonical and CS quantization:

$$\frac{1}{2} = \inf \text{spectrum}\left(\frac{P^2+Q^2}{2}\right) - \inf \text{spectrum}\left(\frac{Q^2}{2}\right) - \inf \text{spectrum}\left(\frac{P^2}{2}\right)$$
$$= \inf \text{spectrum}\left(A_{\frac{p^2+q^2}{2}}\right) - \inf \text{spectrum}\left(A_{\frac{q^2}{2}}\right) - \inf \text{spectrum}\left(A_{\frac{p^2}{2}}\right)\,. \qquad (10)$$

The physical context

- The observed spectrum of diatomic molecules is mainly composed of vibration (near infrared) and rotation (far infrared) spectra. Vibration spectrum occurs mainly for molecules with unequal nuclei.

- When dealing with the electronic transitions of diatomic molecules one considers $E_e \equiv E^{\mathrm{el}} + V_{\mathrm{nuc}}$ where
  - $E^{\mathrm{el}} = E^{\mathrm{el}}(R)$ is an eigenvalue of the electronic part of the Schrödinger equation at fixed nuclei interdistance R, within the framework of the Born-Oppenheimer approximation,
  - and $V_{\mathrm{nuc}} = V_{\mathrm{nuc}}(R)$ is the Coulomb potential of the nuclei.

  Therefore one considers $E_e(R) \equiv U(q)$, with $q \equiv R - R_{\mathrm{eq}}$ (where R_{eq} is the equilibrium interdistance corresponding to the minimum of $E_e(R)$) as the vibrational potential energy of the nuclei issued from a given stable electronic state.

The physical context continued

- The minimum of the lowest (i.e. ground) electronic potential curve **is usually chosen as the origin of the energy scale**.
- **Each** electronic potential curve gives rise to a quantum vibrational Hamiltonian (obtained from canonical quantization) that leads to a spectrum of eigenvalues. The latter are the harmonic ones ($\hbar\omega_e(n+1/2)$) + successive anharmonic corrections ($-\hbar\omega_e x_e(n+1/2)^2 + \hbar\omega_e y_e(n+1/2)^3 + \cdots$), $\omega_e \gg \omega_e x_e \gg \omega_e y_e$, with the notations used in Herzberg [a]). Since different electronic states correspond to different potential curves, the parameters ω_e, x_e, y_e are different in each case.
- The **observed** vibrational spectra correspond **either** to transitions between two vibrational levels corresponding to a **single** electronic state (typically the ground electronic state), **or** to transitions between vibrational levels corresponding to **two** electronic states (the ground electronic state and an excited one).

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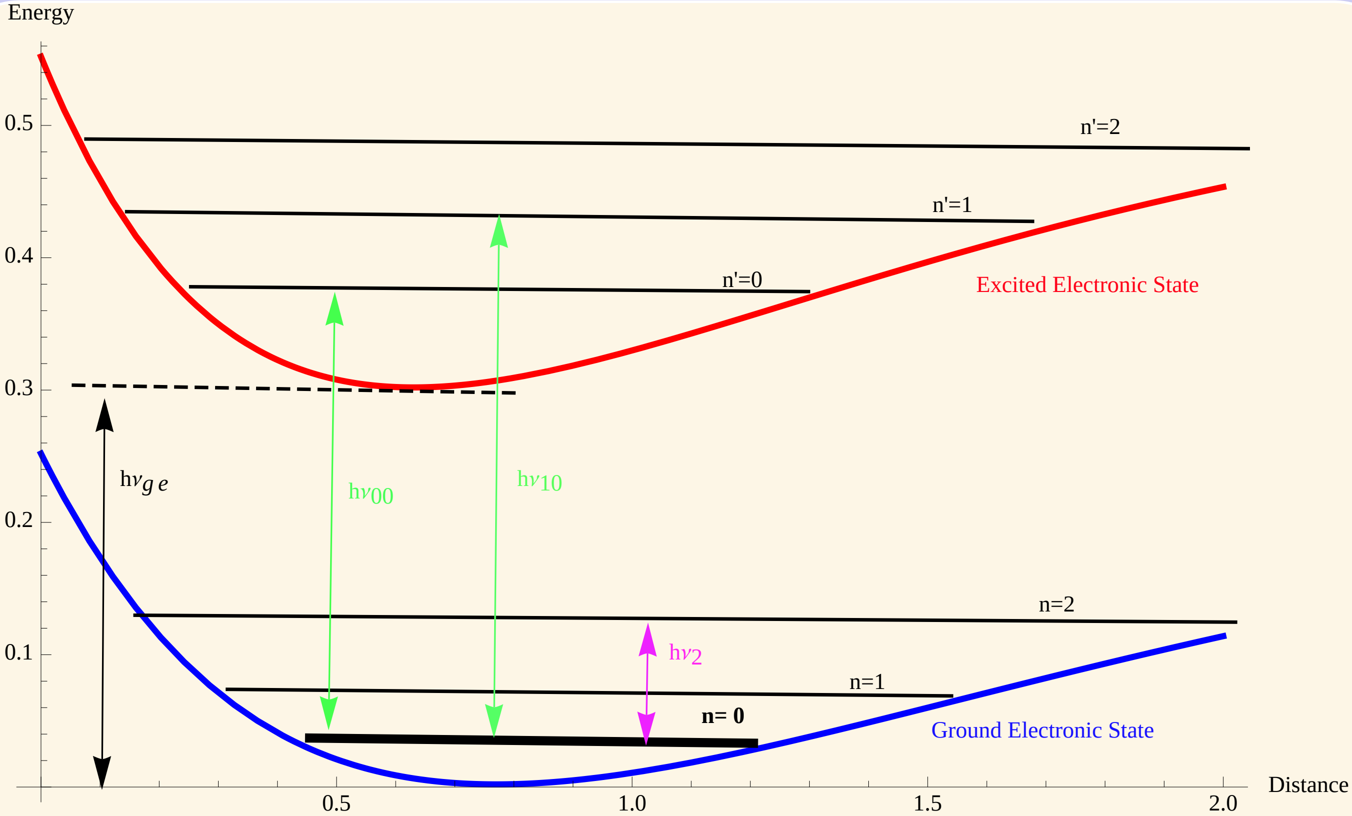
[a] Herzberg, G. 1989, Molecular Spectra and Molecular Structure: Spectra of Diatomic Molecules Krieger Pub Co; 2 edition



Sketch of the energetic diagram (arbitrary units) involving two electronic energetic curves and the corresponding vibrational levels. The black thick line ($n = 0$) represents the quantum ground state vibrational energy of the molecule. Some of the measured energy differences are represented: either issued from a single electronic curve ($h\nu_2$), or issued from two electronic curves ($h\nu_{00}$ and $h\nu_{10}$).

The predicted spectra :
I transitions involving one electronic state

- The vibrational energies E_n are expressed as (with $\hbar = 1$)

$$E_n \equiv G\,(n+1/2) = \omega_e(n+1/2) - \omega_e x_e(n+1/2)^2 + \omega_e y_e(n+1/2)^3 + \cdots\,. \tag{11}$$

- So, the zero-point energy E_0 of the molecule is

$$E_0 = G\,(1/2) = \omega_e/2 - \omega_e x_e/4 + \omega_e y_e/8 + \cdots\,. \tag{12}$$

- If the vibrational energy levels (in this ground electronic state) are referred to this lowest energy level as zero, one writes

$$E_n - E_0 = G\,(n+1/2) - G\,(1/2) \equiv G_0(n) \equiv \omega_0 n - \omega_0 x_0 n^2 + \omega_0 y_0 n^3 + \cdots\,, \tag{13}$$

  where $\omega_0 = \omega_e - \omega_e x_e + \frac{3}{4}\omega_e y_e + \cdots$ etc.

- What is really observed in absorption bands is (in cm^{-1}) $\Delta E_n \equiv E_{n+1} - E_n = \omega_0 - \omega_0 x_0 - 2\omega_0 x_0 n$ (neglecting cubic terms), and $\Delta^2 E_n \equiv \Delta E_{n+1} - \Delta E_n = -2\omega_0 x_0$ (which measures the anharmonicity).

- *Consequently these measurements do not give access to the quantum ground state energy* E_0. But the vibrational constants ω_e and $\omega_e x_e$ (or ω_0 and $\omega_0 x_0$) can be determined from the observed positions of the infrared absorption bands.

The predicted spectra :
II transitions involving two electronic states

- All possible transitions between the different vibrational levels (with and without prime below) corresponding to the two participating electronic states (the ground and the excited electronic potential curves) give rise to the following transition frequencies ν

$$2\pi\nu = E'_{n'} - E_n = 2\pi\nu_{g-e} + G'(n' + 1/2) - G(n + 1/2) \tag{14}$$

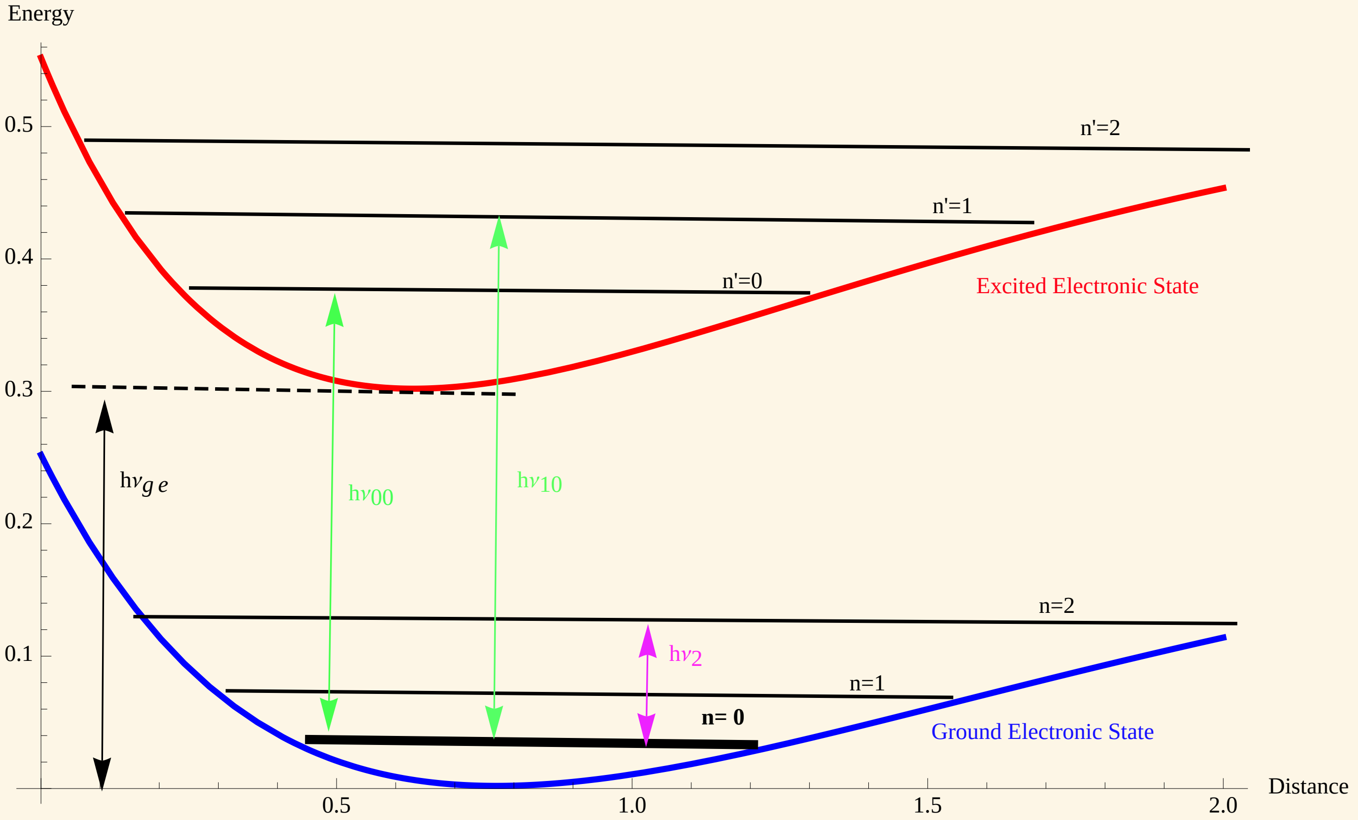
$$\equiv 2\pi\nu_{00} + \omega'_0 n' - \omega'_0 x'_0 n'^2 + \omega'_0 y'_0 n'^3 + \cdots - \left[\omega_0 n - \omega_0 x_0 n^2 + \omega_0 y_0 n^3 + \cdots\right] . \tag{15}$$

- Here $2\pi\nu_{g-e}$ is the difference between the respective minima of the two considered curves $E_e(R)$, and ν_{00} stands for the frequency of the so-called 0-0 band (transition $E_0 \to E'_0$). In the harmonic approximation we have

$$2\pi\nu_{00} = 2\pi\nu_{g-e} + \frac{\omega'_e - \omega_e}{2} . \tag{16}$$

- **It is important to note here that in the earliest Bohr-Sommerfeld quantum theory, this ν_{00} reduces to just ν_{g-e}.**

- We should be also aware that any change in the electronic level implies a change in the constant force of U. Eq. (14) has to be compared with the "band system" obtained from observations and empirically modeled along the same scheme.



Sketch of the energetic diagram (arbitrary units) involving two electronic energetic curves and the corresponding vibrational levels. The black thick line ($n = 0$) represents the quantum ground state energy of the molecule. Some of the measured energy differences are represented: either issued from a single electronic curve ($h\nu_2$), or issued from two electronic curves ($h\nu_{00}$ and $h\nu_{10}$).

The isotopic effect

- When we are in presence of a gas made of isotopic molecules, like $B^{10}O$ – $B^{11}O$, or like HCl^{35} – HCl^{37}, assuming harmonic vibrations, we know that the (classical) vibrational pulsation ω_e is given by $\omega_e = \sqrt{\frac{k}{\mu}}$, where the force constant k is exactly the same for different isotopic molecules, since it is determined by the electronic motion only, whereas the **reduced mass is different**,
$$\frac{\omega_e^{\text{iso}}}{\omega_e} = \sqrt{\frac{\mu}{\mu^{\text{iso}}}} \equiv \rho \,. \tag{17}$$

- Thus, in the case of a transition involving a **single electronic state**, the isotopic effect induces a shift $\Delta\nu$ in absorption band frequencies given by:
$$2\pi\Delta\nu = 2\pi\nu - 2\pi\nu^{\text{iso}} = (1-\rho)\left[(\omega_e - \omega_e x_e(1+\rho))n - \omega_e x_e(1+\rho)n^2\right] \approx (1-\rho)\Delta E_n \,, \tag{18}$$
as long as ρ is only slightly different from 1.

- In the case of transitions involving **two different electronic states**, and specially for ν_{00}, Eq. (16) gives (in the harmonic approximation)
$$2\pi\Delta\nu_{00} = (1-\rho)\frac{\omega_e' - \omega_e}{2} \tag{19}$$

- Such an isotopic displacement for the 0-0 band is actually observed in a number of cases, like for $B^{10}O$ – $B^{11}O$ presented in the next Table. **Thus the existence of the "zero-point" vibration energy (the half quantum) predicted by the canonical quantization is proved**.

Band	Observed Isotopic Displacement $B^{10}O - B^{11}O$ (cm^{-1})	Calculated from Quantum Mechanics (cm^{-1})	Calculated from Bohr-Sommerfeld Theory (cm^{-1})
0-0	-8.6	-9.08	0
1-0	+ 26.7	+ 26.29	+ 35.69
2-0	+ 60.8	+ 60.36	+ 70.09
3-0	+ 93.6	+ 93.14	+ 103.20
4-0	+125.2	+124.63	+135.01

Isotopic displacement $2\pi\Delta\nu_{00}$ in the n'-progression with $n = 0$ of the α band of BO [According to data of Jenkins and McKellar quoted in Herzberg [a]]

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[a] Herzberg book

Conclusion

- From a mathematical point of view, for the problem involving a unique harmonic potential (while, for instance, the most interesting vibrational measurements on diatomic molecules involve two different potentials with anharmonic corrections), and discarding physical parameters, there is no significant difference between canonical and CS quantization.
- Nevertheless one might wonder whether the physical measurements of energies for diatomic molecules are compatible or not with this simplified mathematical treatment. Restore all physical parameters does not change the conclusion, as is shown in the next slides

2. Canonical and coherent state quantization are physically equivalent

In this section all physical parameters are taken into account. We prove the equivalence of the two quantization procedures from a physical point of view.

Coherent states, position and momentum operators

- For defining harmonic coherent states $\mid \xi_{q,p} >$ with parameters in physical classical phase space $\mathcal{P} = \{(q,p) \in \mathbb{R}^2\}$ introduce an arbitrary length scale ℓ and the reduced Planck constant $\hbar$.

- Normalized vectors $\mid \xi_{q,p} >$ are then defined from the states $\mid z >$ as

$$\mid \xi_{q,p} >=\mid \frac{1}{\ell\sqrt{2}} q + i\frac{\ell}{\hbar\sqrt{2}} p > \quad . \tag{20}$$

- The resolution of unity becomes

$$\int_{\mathcal{P}} \frac{dq dp}{2\pi\hbar} \mid \xi_{q,p} >< \xi_{q,p} \mid = \mathbb{I}\,. \tag{21}$$

- CS quantisation of q and p yields $Q = A_q = \frac{\ell}{\sqrt{2}}(a + a^\dagger)$ and $P = A_p = \frac{\hbar}{i\ell\sqrt{2}}(a - a^\dagger)$, with $[Q, P] = i\hbar\mathbb{I}$.

- At this stage ℓ is a free parameter of the theory, since, on a physical point of view, only the spectra of Q and P are observables.

The kinetic energy, the harmonic potential and the harmonic hamiltonian

- We now introduce the mass m of the particle (or the reduced mass of two particles). The quantized kinetic energy $T = A_{p^2/2m}$ is

$$T = A_{p^2/2m} = \frac{P^2}{2m} + \frac{\hbar^2}{4m\ell^2}\,. \tag{22}$$

- The new constant $\frac{\hbar^2}{4m\ell^2}$ must be viewed as an "internal energy" similar to the mc^2 term appearing in a relativistic approach. In fact, if we decide to fix ℓ as being one-half of the Compton length $\ell = \frac{\hbar}{2mc}$ associated to the mass m, we obtain exactly $\frac{\hbar^2}{4m\ell^2} = mc^2$.
- Furthermore the classical harmonic potential is $v(q) = \frac{1}{2}kq^2 \equiv \frac{1}{2}m\omega^2 q^2$ where k is the constant force and ω is the usual vibrational parameter. The CS quantized counterpart $V = A_{v(q)}$ of $v(q)$ reads as

$$V = A_{v(q)} = \frac{1}{2}m\omega^2 Q^2 + \frac{1}{4}m\omega^2\ell^2\,. \tag{23}$$

- Hence, the CS quantization of the classical hamiltonian $h(p,q) = p^2/2m + v(q)$ leads to the quantum hamiltonian H

$$H = A_h = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 Q^2 + \frac{\hbar^2}{4m\ell^2} + \frac{1}{4}m\omega^2\ell^2\,. \tag{24}$$

The kinetic energy, the harmonic potential and the harmonic hamiltonian continued

- If we choose (as it was previously done) the free parameter ℓ as the one-half of the Compton length $\ell = \dfrac{\hbar}{2mc}$, we obtain

$$H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 Q^2 + mc^2 + \gamma\hbar\omega\,. \tag{25}$$

- Here $\gamma = \dfrac{\hbar\omega}{16mc^2}$ is a dimensionless factor expressing the ratio between two typical energies of the model, namely the (non-relativistic) quantum energy $\hbar\omega$ and the rest mass of the particle.
- Since the validity of the classical hamiltonian $h(p, q)$ is restricted to the non-relativistic domain, and since in this case the ratio γ is completely negligible, we obtain

$$H \simeq \frac{P^2}{2m} + \frac{1}{2}m\omega^2 Q^2 + mc^2\,. \tag{26}$$

- This is exactly the quantum hamiltonian yielded by canonical quantization, up to the very large (and physically correct, even if usually omitted), constant mc^2, i.e. the energy proper to and only to the particle.
- Since only **energy differences** (between levels of a same spectrum or two different spectra) **relative to (and only to) a given particle** are concerned in measuring the vibrational spectra of diatomic molecules, then the constant term $\dfrac{\hbar^2}{4m\ell^2}$ (identical for the two spectra and chosen here as being mc^2) is dropped.

Conclusion

- Therefore if the potentials are perfectly harmonic, the previous reasoning shows that for a suitable choice of the free parameter ℓ, no **measurable** difference exists between the predictions of canonical quantization and CS quantization.
- [This reasoning includes the isotopic effect, since the latter corresponds to the comparison between two energy differences, each of them being obtained on a single particle].
- Of course we can wonder if the anharmonic character of the potentials modifies this result.
- Extension of the reasoning to WH quantization based on an arbitrary $\varpi(z)$ should be done!

Comments

- Actually the previous reasoning does not prove that the free parameter ℓ *is* one-half of the Compton length (this choice has been done for convenience, in order to obtain concrete formula).
- It allows only to conclude that if ℓ is chosen small enough, possibly particle dependent, *but not potential dependent*, then the only physical difference between canonical and CS quantization (in the harmonic case) is the introduction of a (very large) proper energy for the particle, the latter **being not measurable** in the context of non-relativistic dynamics.
- The "non-measurability" of this proper energy (in the non-relativistic framework) can be physically justified by the absolute and complete conservation of this energy for a given particle (conservation in the whole space-time, and then in all possible interactions of the particle during "its life"). For a given particle, within the non-relativistic framework, only **energy variations are measurable**.
- In fact through the parameter ℓ, we recover the old idea of "proper wave function" of a particle first introduced by Lande [a] and Born [b] to describe elementary particles that are not pointlike.

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[a] Lande, 1939

[b] Born, 1939

A generalization to anharmonic potentials

- In the following we denote the constant energetic term by $\mathcal{E}_0(\ell) = \dfrac{\hbar^2}{4m\ell^2}$. For a general classical potential $V(q)$ we can prove that the corresponding operator $A_{V(q)}$ reads as a multiplication operator defined by the following convolution:

$$A_{V(q)} = \tilde{V}(Q) \quad \text{with} \quad \tilde{V}(q) = \int_{\mathbb{R}} V(q-x)e^{-x^2/\ell^2}\frac{\mathrm{d}x}{\sqrt{\pi\ell^2}}\,. \tag{27}$$

- This expression can be easily obtained by using the well-known "Gaussian x-representation" $\langle\, \delta_x \,|\, \xi_{p,q} \,\rangle$ of coherent states and then by calculating the "matrix elements" $< \delta_x \mid A_{V(q)} \mid \delta_y >$.

- For ℓ small enough, we have $e^{-x^2/\ell^2}/\sqrt{\pi\ell^2} \simeq \delta(x)$, and then we recover $\tilde{V}(Q) \simeq V(Q)$. The first correction is given by a second derivative of V

$$\tilde{V}(Q) \simeq V(Q) + \frac{\ell^2}{4}V''(Q)\,. \tag{28}$$

- Therefore the quantum hamiltonian H is

$$H \simeq \frac{P^2}{2m} + V(Q) + \frac{\ell^2}{4}V''(Q) + \mathcal{E}_0(\ell)\,. \tag{29}$$

- Hence, we can generalize the result of the previous section (when ℓ is small enough) to anharmonic potentials.

- If ℓ is chosen as one-half of the Compton length, the term $\frac{\ell^2}{4}V''(Q)$ *looks like* a well-known relativistic correction obtained from the Foldy-Wouthuysen transformation, namely the so-called Darwin term.

Conclusion

The detailed analysis exposed above shows that it is impossible to distinguish between the predictions issued from canonical quantization and those issued from CS quantization if we just use data from vibrational spectra. In fact as long as the only observables that are taken into account are position, momentum and energy, the predictions of the two procedures are equivalent. This does not mean that the procedures are equivalent over the theoretical set of all mathematical observables (functions on phase space); but this set is much larger than the set of "real" observables that can be effectively measured.