Rayleigh-Ritz and Gibbs-Bogoliubov

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The Rayleigh-Ritz theorem states that the ground state energy of a quantum system is a lower bound for the expectation value of the Hamiltonian in any state. A proof for pure and mixed trial states is presented. The Gibbs-Bogoliubov inequality states that the free energy of a system is bounded above by a (quasi) free energy expression using any trial state. Its quantum version is proved by using (and also proving) the quantum version of the Gibbs inequality. The Rayleigh-Ritz theorem can be viewed as the zero temperature limit of the Gibbs-Bogoliubov inequality.

I. RAYLEIGH-RITZ VARIATIONAL PRINCIPLE

The Rayleigh-Ritz-theorem states the almost obvious fact that *the expectation value of the Hamiltonian in any arbitrary state cannot be smaller than the ground state energy*. This is "illustrated" graphically in Fig. 1. In the following we formulate the theorem first for *pure* states and then slightly generalize to *mixed* states, since the latter are important in statistical physics [1]

A. Rayleigh Ritz for pure states

Theorem 1 *Let $\hat{H}$ be a Hamiltonian acting on a Hilbert space $\mathscr{H}$ which has a discrete spectrum and ground state energy E_0. Furthermore, let $|\psi\rangle \in \mathscr{H}$ be any* pure *quantum state. Then*

$$\langle \hat{H} \rangle \;\equiv\; \langle\psi|\hat{H}|\psi\rangle \;\geq\; E_0. \tag{1}$$

Proof: Let $\{|n\rangle\}$ be the set of state vectors corresponding to the energy eigenstates of the Hamiltonian $\hat{H}$. Since these form an orthonormal [2] basis of $\mathscr{H}$, we can write $|\psi\rangle$ as the expansion $\sum_n \psi_n|n\rangle$, and it follows

$$\begin{aligned}
\langle \hat{H}\rangle - E_0 &= \langle\psi|(\hat{H}-E_0)|\psi\rangle \\
&= \sum_{m,n} \psi_m^*\psi_n \langle m|(\hat{H}-E_0)|n\rangle \\
&= \sum_{m,n} \psi_m^*\psi_n \underbrace{\langle m|n\rangle}_{\delta_{mn}} (E_n - E_0) \\
&= \sum_n \underbrace{|\psi_n|^2}_{\geq 0} \underbrace{(E_n-E_0)}_{\geq 0} \;\geq\; 0. \qquad \square
\end{aligned}$$

B. Rayleigh Ritz for mixed states

Theorem 2 *Let $\hat{H}$ be a Hamiltonian acting on a Hilbert space $\mathscr{H}$ which has a discrete spectrum and ground state energy E_0. Furthermore, let $\hat{W}$ be any quantum state on $\mathscr{H}$. Then*

$$\langle \hat{H} \rangle \;\equiv\; \mathrm{Tr}\,(\hat{W}\hat{H}) \;\geq\; E_0. \tag{2}$$

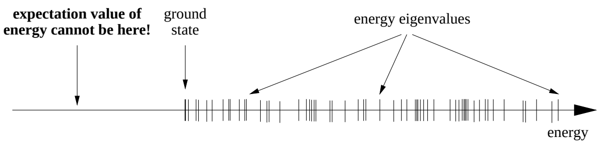

FIG. 1: "Graphical illustration" of the Rayleigh-Ritz theorem: The expectation value of the Hamiltonian in any arbitrary state cannot be smaller than the ground state energy.

Proof: We can write $\hat{W}$ as a convex combination of eigenstates $\hat{W}_n = |n\rangle\langle n|$ of $\hat{H}$, *i.e.*, $\hat{W} = \sum_n p_n \hat{W}_n$, with $\sum_n p_n = 1$ [3]. We now have

$$\begin{aligned}
\langle \hat{H}\rangle - E_0 &= \mathrm{Tr}\,\big(\hat{W}(\hat{H}-E_0)\big) \\
&= \sum_{m,n} \langle m|p_n|n\rangle\langle n|(\hat{H}-E_0)|m\rangle \\
&= \sum_{m,n} |\underbrace{\langle m|n\rangle}_{\delta_{nm}}|^2 p_n (E_m - E_0) \\
&= \sum_n p_n (E_n - E_0) \;\geq 0. \qquad \square
\end{aligned}$$

II. GIBBS-BOGOLIUBOV INEQUALITY

The Rayleigh-Ritz theorem refers to the ground state of an isolated quantum system. What if instead we have a quantum system coupled to a thermal heat bath, such that the system is not in the ground state $|0\rangle$ but instead in the canonical state $\hat{W}_{\mathrm{can}} := \mathrm{e}^{-\beta\hat{H}}/Z$ with $Z = \mathrm{Tr}\,\mathrm{e}^{-\beta\hat{H}}$? In that case we have a generalization of the Rayleigh-Ritz theorem, which is termed the Gibbs-Bogoliubov inequality:

Theorem 3 *Let $\hat{H}$ be a Hamiltonian acting on a Hilbert space $\mathscr{H}$. Furthermore, let $F = -k_{\mathrm{B}}T\log\mathrm{Tr}\,\mathrm{e}^{-\beta\hat{H}}$ be the canonical free energy and $\hat{W}_{\mathrm{t}}$ some arbitrary ("trial") quantum state on $\mathscr{H}$ with (von Neumann) entropy $S_{\mathrm{t}} = -k_{\mathrm{B}}\mathrm{Tr}\,(\hat{W}_{\mathrm{t}}\log\hat{W}_{\mathrm{t}})$. Denote the expectation value of the Hamiltonian in the state $\hat{W}_{\mathrm{t}}$ by $\langle\hat{H}\rangle_{\mathrm{t}} = \mathrm{Tr}\,(\hat{W}_{\mathrm{t}}\hat{H})$. Then*

$$F \;\leq\; \langle\hat{H}\rangle_{\mathrm{t}} - TS_{\mathrm{t}}. \tag{3}$$

For the proof of this theorem we will make use of the Gibbs-inequality, which we intend to present and proof first:

Theorem 4 (Gibbs-inequality) *Let $\hat{W}$ and $\hat{W}'$ be any two arbitrary quantum states acting on a Hilbert space $\mathscr{H}$. We then have the inequality*

$$\mathrm{Tr}\,(\hat{W}\log\hat{W}) \;\geq\; \mathrm{Tr}\,(\hat{W}\log\hat{W}') \qquad (4)$$

Proof: (Gibbs inequality) Write the states $\hat{W}$ and $\hat{W}'$ using an expansion in an arbitrary basis $\{|n\rangle\}$ of the Hilbert space:

$$\hat{W} \;=\; \sum_n p_n|n\rangle\langle n| \quad \text{and} \quad \hat{W}' \;=\; \sum_n p'_n|n\rangle\langle n|.$$

We then have

$$\begin{aligned}\hat{W}\log\hat{W}' - \hat{W}\log\hat{W} \;&= \\ = \sum_{m,n}&\Big[p_n|n\rangle\langle n|\log p'_m|m\rangle\langle m| - p_n|n\rangle\langle n|\log p_m|m\rangle\langle m|\Big] \\ = \sum_n&\big[p_n\log p'_n - p_n\log p_n\big]|n\rangle\langle n|.\end{aligned}$$

From this follows by performing the trace and using the elementary inequality $\log x \leq x-1$

$$\begin{aligned}\mathrm{Tr}\,(\hat{W}\log\hat{W}') - \mathrm{Tr}(\hat{W}\log\hat{W}) \;&= \\ = \sum_n&\big[p_n\log p'_n - p_n\log p_n\big] \\ = \sum_n& p_n\log\frac{p'_n}{p_n} \;\leq\; \sum_n\big[p'_n - p_n\big] \;=0 \qquad \square\end{aligned}$$

We are now in the position to prove the Gibbs-Bogoliubov inequality.

Proof: (Gibbs-Bogoliubov inequality) In the Gibbs inequality choose $\hat{W}'$ as the canonical state $\hat{W}_{\mathrm{can}} = \mathrm{e}^{-\beta\hat{H}}/Z$ and choose $\hat{W}$ as the trial state $\hat{W}_{\mathrm{t}}$. It then follows that

$$\begin{aligned}TS_{\mathrm{t}} \;&=\; -k_{\mathrm{B}}T\;\mathrm{Tr}\,(W_{\mathrm{t}}\log W_{\mathrm{t}}) \\ &\leq\; -k_{\mathrm{B}}T\;\mathrm{Tr}\,(W_{\mathrm{t}}\log W_{\mathrm{can}}) \\ &=\; -k_{\mathrm{B}}T\;\mathrm{Tr}\Big(\hat{W}_{\mathrm{t}}\big(-\beta H - \log Z\big)\Big) \\ &=\; \mathrm{Tr}\,(\hat{W}_{\mathrm{t}}\hat{H}) - F. \qquad \square\end{aligned}$$

The Gibbs-Bogoliubov inequality is extremely useful in statistical physics, since it permits an estimation of the real free energy of any system by using a "trial" state $\hat{W}_{\mathrm{t}}$ that may be much easier to handle than the actual canonical state. For instance, in systems comprising many interacting particles the canonical state is extremely complicated because all particles are *correlated* and the trace is therefore essentially impossible to perform. However, if one uses as a trial state a *product* state, all these correlations disappear. This is often the most beautiful way to derive a mean-field theory.

We finally remark that both the Gibbs- as well as the Gibbs-Bogoliubov-inequality remain valid in *classical* statistical physics. All one has to do is to replace the quantum state $\hat{W}$ by a classical state $w(p,q)$ (*i.e.*, a probability density on phase space) and the trace over the Hilbert space $\mathscr{H}$ by the integral over phase space Γ:

$$\int_\Gamma \mathrm{d}\Gamma\; w(p,q)\log w(p,q) \geq \int_\Gamma \mathrm{d}\Gamma\; w(p,q)\log w'(p,q)$$

and

$$F \;\leq\; \langle H\rangle_{\mathrm{t}} - TS_{\mathrm{t}},$$

where we have $\mathrm{d}\Gamma = \mathrm{d}p_1\ldots\mathrm{d}p_N\,\mathrm{d}q_1\ldots\mathrm{d}q_n/(2\pi\hbar)^N$, and of course $\langle H\rangle_{\mathrm{t}} = \int_\Gamma \mathrm{d}\Gamma\; w_{\mathrm{t}}(p,q)H(p,q)$ and $S_{\mathrm{t}} = -k_{\mathrm{B}}\int_\Gamma \mathrm{d}\Gamma\; w_{\mathrm{t}}(p,q)\log w_{\mathrm{t}}(p,q)$. The proof is quite analogous (actually, it is easier, since no expansion in eigenstates is necessary).

III. GIBBS-BOGOLIUBOV IN THE LIMIT $T \to 0$

We will now show that in the limit $T \to 0$ the Gibbs-Bogoliubov inequality reduces to the Rayleigh-Ritz theorem. For this to see one only has to realize that at zero temperature the system is in its ground state and the free energy is equal to the energy (since the entropy term $-TS$ vanishes). Hence, the left hand side of the Gibbs-Bogoliubov inequality (3) is equal to the ground state energy, while the right hand side becomes the expectation value of the energy in some arbitrary quantum state $\hat{W}_{\mathrm{t}}$. This, however, is just the Rayleigh-Ritz theorem in the form of Eqn. (2).

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[1] A general (mixed) quantum state is a self-adjoint, positive operator on a Hilbert space $\mathscr{H}$ with trace 1: $\hat{W}^\dagger = \hat{W} > 0$ and $\mathrm{Tr}\,\hat{W} = 1$. If this state is *pure*, then there exists a *state vector* $|\psi\rangle \in \mathscr{H}$ such that $\hat{W} = |\psi\rangle\langle\psi|$.

[2] If degeneracy occurs, the eigenstates may not initially be orthogonal, but they can always be orthogonalized.

[3] The p_n specify the composition of the mixture, *i.e.*, with what fraction state $\hat{W}_n$ contributes to the mixture. Note that a mixture is an *incoherent* superposition of quantum states, since contrary to the *state vector* $|n\rangle$ the *state* $\hat{W}_n = |n\rangle\langle n|$ does not contain any phase information. In other words, phase differences between two state vectors $|m\rangle$ and $|n\rangle$ are invisible when looking at the states $\hat{W}_m$ and $\hat{W}_n$.