The Hellmann-Feynman theorem at finite temperature

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We present a simple derivation of the Hellmann-Feynman theorem at finite temperature. We illustrate its validity by considering three relevant examples which can be used in quantum mechanics lectures: the one-dimensional harmonic oscillator, the one-dimensional Ising model and the Lipkin model. We show that the Hellmann-Feynman theorem allows one to calculate expectation values of operators that appear in the Hamiltonian. This is particularly useful when the total free energy is available, but there is no direct access to the thermal average of the operators themselves.

I. INTRODUCTION

The Hellmann-Feynman (HF) theorem at zero temperature is a very useful tool in quantum mechanics. Its most important application involves the calculation of expectation values of operators contained in the Hamiltonian. The theorem is often introduced in undergraduate quantum mechanics courses, and has been derived and generalized in different ways. The HF is closely connected to the virial theorem. In the context of perturbation theory, Epstein showed that the HF theorem provides a consistent picture of wavefunction renormalization. It was later used to generate Rayleigh-Schrödinger perturbation theory corrections. In its simplest version, the theorem is used for non-degenerate states. Generalizations to degenerate subspaces also exist. The theorem is versatile and has been extended to off-diagonal expectation values, to Gamow states, to linear superpositions of energy eigenstates and to cases where the domain of definition of the Hamiltonian depends on a parameter. Analogues of the theorem can be found in classical systems, and a time-dependent extension has been formulated too.

Applications of the theorem span a large number of sub-fields. In atomic physics, the HF theorem can be used to find closed expressions for useful expectation values. In quantum chemistry, the HF theorem has been used to evaluate molecular forces and to calculate Coulomb interaction energies. The quark mass dependence in some hadronic systems can be accessed through the HF theorem. Efficient implementations of the HF theorem in diffusion Monte Carlo simulations provide direct access to kinetic and potential energies of bosonic systems. In nuclear physics, the theorem has been used recently to extract contributions of the nuclear force to the nuclear symmetry and spin symmetry energies.

In contrast to these zero-temperature cases, the use of the HF theorem at finite temperature is much more scarce. The first derivation that we are aware of is provided in Ref. This was followed by independent derivations in Refs. and each with a somewhat different focus. When it comes to actual applications, the HF theorem is rarely employed at finite temperature. Exceptions include the calculation of correlation functions in 1D Bose gases and the evaluation of specific matrix elements in lattice QCD. In heavy-ion physics, the HF theorem provides a direct link between thermodynamical consistency and quasi-particle descriptions. In the context of strongly correlated fermionic systems, the adiabatic sweep relations derived by Tan arise naturally in a HF formulation, and have been used to study finite temperature systems in Ref. The theorem has been used to link thermodynamical properties to microscopic density matrices in the context of quantum phase transitions.

The scope of the present paper is to present a simple derivation of the HF theorem at finite temperature, as a useful resource in teaching quantum mechanics at finite temperature. We complement the derivation of the
II. THE HELLMANN-FEYNMAN THEOREM

A. Zero temperature

The HF theorem allows one to determine the expectation value of an operator contained in the Hamiltonian for a given non-degenerate eigenstate. To derive the theorem, one defines a parametric, \( \lambda \)-dependent, Hamiltonian, \( H^\lambda \). In the examples presented in this paper, we make use of a linear dependence in \( \lambda \),

\[
H^\lambda = H_0 + \lambda H_1, \tag{1}
\]

but this does not need to be the case. For \( \lambda = 1 \), the Hamiltonian in Eq. (1) is automatically decomposed in two pieces, \( H = H_0 + H_1 \), where \( H_1 \) is the operator for which we want to calculate the expectation value. Typically, these operators are the kinetic or the potential energies but, as we shall see in the following, other options arise depending on the model and the corresponding Hamiltonian.

The \( n^{th} \)-eigenvalue of \( H^\lambda \), \( E_n^\lambda \), is the solution of the eigenvalue problem

\[
H^\lambda |\psi_n^\lambda\rangle = E_n^\lambda |\psi_n^\lambda\rangle. \tag{2}
\]

Hereafter, all observables denoted with a \( \lambda \) superscript are to be understood as expectation values over \( \lambda \)-dependent states, \( |\psi_n^\lambda\rangle \). For a linear parametric dependence on \( \lambda \), Eq. (1), the zero-temperature HF theorem states that one can evaluate the expectation value \( \langle \psi_n | H_1 | \psi_n \rangle \) from the derivative with respect to \( \lambda \) of the corresponding eigenenergies,

\[
\langle \psi_n | H_1 | \psi_n \rangle = \left. \frac{dE_n^\lambda}{d\lambda} \right|_{\lambda=1}. \tag{3}
\]

The theorem is useful because a direct calculation of the expectation value on the left hand side is sometimes more cumbersome than the direct evaluation of the energy derivative on the right hand side.

We now proceed to prove this zero-temperature result, as this sets the ground for the finite temperature discussion. The proof has been discussed in many standard quantum mechanics books, and it stems from a careful analysis of the derivative of the eigenvalue defined by Eq. (2). The derivative is in fact decomposed in three terms,

\[
\frac{dE_n^\lambda}{d\lambda} = \frac{d}{d\lambda} \left[ \langle \psi_n^\lambda | H^\lambda | \psi_n^\lambda \rangle \right] = \left( \frac{d}{d\lambda} \langle \psi_n^\lambda | H^\lambda | \psi_n^\lambda \rangle \right) + \langle \psi_n^\lambda | H^\lambda \left( \frac{d}{d\lambda} | \psi_n^\lambda \rangle \right).
\]

Taking into account that \( |\psi_n^\lambda\rangle \) is an eigenvector of \( H^\lambda \), the first and third terms can be combined to yield

\[
\frac{dE_n^\lambda}{d\lambda} = E_n^\lambda \left[ \delta_{\lambda 1} \langle \psi_n^\lambda | H^\lambda | \psi_n^\lambda \rangle + \langle \psi_n^\lambda | \frac{dH^\lambda}{d\lambda} | \psi_n^\lambda \rangle \right]. \tag{5}
\]

The HF theorem, Eq. (3), is obtained for a linear parametric dependence, Eq. (1), and for \( \lambda = 1 \). In particular, we note that the relation holds for any state, \( n \), and is true for the ground state, \( n = 0 \).

B. Finite temperature

The HF theorem at finite temperature has been much less discussed in the literature. In the following, we employ the canonical ensemble in our derivation. Starting, again, from a \( \lambda \)-dependent parametric Hamiltonian, we define a \( \lambda \)-dependent density matrix operator,

\[
\rho^\lambda = e^{-\beta H^\lambda}, \tag{7}
\]

where \( \beta = 1/T \) is the inverse of the temperature. The partition function \( Z^\lambda \) is defined as the trace of \( \rho^\lambda \), and can be evaluated in the basis of eigenvectors of \( H^\lambda \),

\[
Z^\lambda = \text{Tr} \rho^\lambda = \sum_n e^{-\beta E_n^\lambda}. \tag{8}
\]

From the partition function, one can evaluate relevant thermodynamical potentials like the average thermal energy,

\[
E^\lambda = -\frac{\partial}{\partial \beta} \ln Z^\lambda. \tag{9}
\]

Further, we note that the free energy is given by the expression

\[
F^\lambda = -\frac{1}{\beta} \ln Z^\lambda = -T \ln \sum_n e^{-\beta E_n^\lambda}, \tag{10}
\]

and the entropy, in turn, is given by

\[
S^\lambda = -\frac{\partial F^\lambda}{\partial T}. \tag{11}
\]
The derivative of $F^\lambda$ with respect to $\lambda$ yields
\begin{equation}
\frac{\partial F^\lambda}{\partial \lambda} = \frac{1}{Z^\lambda} \sum_n e^{-\beta E_n^\lambda} \frac{dE_n^\lambda}{d\lambda}.
\end{equation}
The eigenvalue derivatives, $dE_n^\lambda/d\lambda$, are independent of the temperature and given by Eq. (6). As a consequence, the derivative of the free energy can be expressed as a thermal ensemble average of $\partial H^\lambda/\partial \lambda$,
\begin{equation}
\frac{\partial F^\lambda}{\partial \lambda} = \frac{1}{Z^\lambda} \sum_n e^{-\beta E_n^\lambda} \langle \psi_n^\lambda | \partial H^\lambda/\partial \lambda | \psi_n^\lambda \rangle
= \langle \frac{\partial H^\lambda}{\partial \lambda} \rangle_T.
\end{equation}
at a given value of $\lambda$. In particular, for a linear parametric dependence, Eq. (1), and for $\lambda = 1$, one recovers the thermal average of $H_1$ at a temperature $T$, $(H_1)_T$:
\begin{equation}
\frac{\partial F^\lambda}{\partial \lambda} \bigg|_{\lambda=1} = \frac{1}{Z^\lambda} \sum_n e^{-\beta E_n} \langle \psi_n | H_1 | \psi_n \rangle = (H_1)_T.
\end{equation}
Note that this expression is very similar to the HF theorem at $T = 0$, Eq. (3), but replacing the energy, $E^\lambda$, with the free energy, $F^\lambda$. This is the main result of this paper, which we take as the generalization of the HF theorem to finite temperature. We will use this result in the following sections to illustrate the usefulness of the theorem.

An additional useful result can be derived as a corollary. At finite temperature, the energy and the free energy differ by a factor proportional to the entropy. At arbitrary $\lambda$, the difference is given by the expression
\begin{equation}
F^\lambda = E^\lambda - T S^\lambda.
\end{equation}
This relation suggests that one can also find a HF-like expression for the entropy. In fact, taking the derivative with respect to $\lambda$ of Eq. (11), one finds
\begin{equation}
\frac{\partial S^\lambda}{\partial \lambda} = - \frac{\partial^2 F^\lambda}{\partial \lambda \partial T}.
\end{equation}
Switching the order of the derivatives and using Eq. (14), we obtain
\begin{equation}
\frac{\partial S^\lambda}{\partial \lambda} \bigg|_{\lambda=1} = - \frac{\partial (H_1)_T}{\partial T}.
\end{equation}
This expression suggests that the entropy of the system is directly connected to the temperature derivatives of thermal expectation values of $H_1$. This is to a certain extent unexpected, because the entropy itself is not directly related to thermal averages of parts of the Hamiltonians.

In the following three sections, we illustrate the HF theorem with three different Hamiltonians and settings that are often discussed in quantum-mechanics teaching. Each example shows a different application of the theorem to compute different contributions to the system’s energies or thermodynamical potentials.

### III. HARMONIC OSCILLATOR

We start with the textbook example of a one-dimensional harmonic oscillator (h.o.). A unique advantage of this example is that it can be treated analytically at finite temperature. We use h.o. units, in which the Hamiltonian reads,
\begin{equation}
H = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{\lambda}{2} x^2.
\end{equation}
The eigenvalues are $E_n = (n + \frac{1}{2})$ for $n = 0, 1, 2, \ldots$

The application of the HF theorem at zero temperature is straightforward, and allows a direct evaluation of the h.o. potential term. One defines the $\lambda$-dependent Hamiltonian
\begin{equation}
H^\lambda = -\frac{1}{2} \frac{d^2}{dx^2} + \lambda \frac{x^2}{2},
\end{equation}
so that $H_0$ is the kinetic term and $H_1$ is the h.o. potential.

In practice, $\lambda$ renormalizes the h.o. frequency by a factor $\sqrt{\lambda}$, and consequently the eigenvalues of $H^\lambda$ are given by the expression $E_n^\lambda = (n + \frac{1}{2}) \sqrt{\lambda}$. At zero temperature, the HF theorem is useful in computing the expectation value of the harmonic potential in any eigenstate:
\begin{equation}
\langle \psi_n | \frac{x^2}{2} | \psi_n \rangle = \frac{\partial E_n^\lambda}{\partial \lambda} \bigg|_{\lambda=1} = \left( n + \frac{1}{2} \right) \frac{1}{2 \sqrt{\lambda}} \bigg|_{\lambda=1}
= \frac{1}{2} \left( n + \frac{1}{2} \right).
\end{equation}
This expression is in agreement with the virial theorem.

At finite temperature, the expressions for the partition function associated to $H$ can be found in statistical mechanics textbooks,
\begin{equation}
Z = \sum_{n=0}^{\infty} e^{-\beta (n + \frac{1}{2})} = \frac{1}{2 \csc \left( \frac{\beta}{2} \right)}.
\end{equation}
From the partition function, one can derive analytical expressions for the free energy
\begin{equation}
F = -\frac{1}{\beta} \ln Z = \frac{1}{2} + \frac{1}{\beta} \ln (1 - e^{-\beta});
\end{equation}
the average thermal energy,
\begin{equation}
E = - \frac{\partial}{\partial \beta} \ln Z = \frac{1}{2} + \frac{e^{-\beta}}{1 - e^{-\beta}};
\end{equation}
and the entropy,
\begin{equation}
S = - \ln (1 - e^{-\beta}) + \frac{\beta e^{-\beta}}{1 - e^{-\beta}}.
\end{equation}

Similar expressions hold for the thermodynamical potentials associated to the parametric Hamiltonian $H^\lambda$. The associated free energy is given by
\begin{equation}
F^\lambda = \frac{\sqrt{\lambda}}{2} + \frac{1}{\beta} \ln (1 - e^{-\beta \sqrt{\lambda}}).
\end{equation}
This expression can then be used in the finite temperature HF theorem, Eq. (14), to find the thermal average of the harmonic potential:

$$\langle x^2/2 \rangle_T = \left. \frac{\partial F^\lambda}{\partial \lambda} \right|_{\lambda=1} = \frac{1}{4} + \frac{1}{2} \frac{1}{1 - e^{-\beta}}. \quad (26)$$

This result agrees with the finite temperature virial theorem, which states that the potential and the kinetic energies each contribute a half of the total energy, Eq. (23):

$$\langle x^2/2 \rangle_T = \frac{1}{2} E. \quad (27)$$

Panel (a) of Fig. 1 shows the thermodynamical potentials $E$ (solid line) and $F$ (dashed line), as well as the thermal expectation value of $x^2/2$ (dotted line) for a one dimensional harmonic oscillator as a function of temperature. As expected, both $E$ and $F$ tend to 1/2 at very low temperatures. In contrast, for large $T$, classical statistics dictates that $E \xrightarrow{T \to 1} 0.5$ and $F \xrightarrow{T \to 1} -T \ln T$. For all values of temperature, we find that Eq. (27) holds, in agreement with the virial theorem.

Further, we report in panel (b) of Fig. 1 the two derivatives $\partial E^\lambda/\partial \lambda |_{\lambda=1}$ (solid line) and $\partial F^\lambda/\partial \lambda |_{\lambda=1}$ (dashed line) as a function of the temperature. Notice that $\partial F^\lambda/\partial \lambda |_{\lambda=1}$ coincides with the thermal average $\langle x^2/2 \rangle_T$ shown in panel (a). In contrast, the corresponding derivative of the energy is not related to a thermal average of the Hamiltonian. The asymptotic behaviours of these derivatives are known. When $T \to 0$, both derivatives tend to the same value, $\partial E^\lambda/\partial \lambda |_{\lambda=1} = \partial F^\lambda/\partial \lambda |_{\lambda=1} \to 1/4$, which is precisely the expectation value of $x^2/2$ on the zero-temperature ground state, $n = 0$. The classical limit for the two derivatives is however very different. For $T \to \infty$, $\partial E^\lambda/\partial \lambda |_{\lambda=1} \to 0$ and is therefore negligible. The derivative of the free energy, however, is a linearly increasing function of $T$, $\partial F^\lambda/\partial \lambda |_{\lambda=1} \to T/2$.

The h.o. case also allows for an explicit analytical test of Eq. (17). On the other hand, the derivative of the thermal average of the harmonic potential can be explicitly calculated,

$$\frac{\partial}{\partial T} \langle H_1 \rangle_T = \frac{\partial}{\partial T} \left( \frac{x^2}{2} \right)_T = \frac{\beta^2}{2} \frac{e^{-\beta}}{(1 - e^{-\beta})^2}. \quad (28)$$

On the other hand, $S^\lambda$ is written as,

$$S^\lambda = - \ln \left( 1 - e^{-\beta\sqrt{\lambda}} \right) + \sqrt{\lambda} \beta \frac{e^{-\beta\sqrt{\lambda}}}{1 - e^{\beta\sqrt{\lambda}}}, \quad (29)$$

and therefore,

$$\left. \frac{\partial S^\lambda}{\partial \lambda} \right|_{\lambda=1} = -\beta^2 \frac{1}{2} \frac{e^{-\beta}}{(1 - e^{-\beta})^2}, \quad (30)$$

in agreement with Eq. (17). This function is reported in the solid line of panel (c) of Fig. 1. We note that this is a monotonously decreasing function of temperature (notice the minus sign in the figure legend), which goes to zero at very low temperatures. In contrast, in the classical limit, the function asymptotically tends to $-\frac{1}{2}$ (dotted line).

**FIG. 1.** (a) Energy $E$ (solid line), free energy $F$ (dashed line) and $\langle x^2/2 \rangle_T$ (dotted line) as a function of temperature for a one dimensional harmonic oscillator. The solid line, $E_T = \frac{x^2}{2}$, illustrates the classical limit of the potential energy. (b) Derivative of $E^\lambda$ (solid line) and $F^\lambda$ (dotted line) with respect to $\lambda$ at $\lambda = 1$ as a function of temperature. (c) Minus the derivative of $S^\lambda$ with respect to $\lambda$ at $\lambda = 1$ as a function of temperature (solid line). The sign is chosen so this expression coincides with $\left. \frac{\partial F^\lambda}{\partial \lambda} \right|_{\lambda=1}$. The dotted line corresponds to the asymptotic value $\left. \frac{\partial S^\lambda}{\partial \lambda} \right|_{\lambda=1} \to -1/2$. 
By virtue of Eq. (28), this implies that the classical limit of the potential energy is $T/2$, as reported in panel (a).

IV. ISING MODEL

The second example we consider is the Ising model,\textsuperscript{39} which is also discussed in many textbooks of statistical mechanics\textsuperscript{41} in connection with the study of ferromagnetic materials and phase transitions. The HF theorem in this model can be used to estimate different terms of the Hamiltonian which have physical relevance. While analytical expressions for the partition function are available, our discussion is based on numerical results for brevity.

The Hamiltonian of the one-dimensional Ising model reads

$$H = -J \sum_{\langle i,j \rangle} s_i s_j - \lambda \sum_i s_i.$$  \hspace{1cm} (31)

Here, $J$ is the coupling constant between two spins and the symbol $\langle i,j \rangle$ indicates that the spins interact only with their nearest neighbours. $s_i$ are a collection of spin variables which can take values of $\pm 1$. We consider a one dimensional chain of $N$ spins with periodic boundary conditions. The Hamiltonian describes a ferromagnetic (antiferromagnetic) system for $J < 0$ ($J > 0$). $\lambda$ defines the strength of an external (magnetic) field.

At zero temperature, the ground state corresponds to a configuration in which all the spins are pointing in the same direction. The finite temperature discussion is framed by the partition function, which in this case is framed by the partition function, which in this case and considering periodic boundary conditions, is given by\textsuperscript{41,42}

$$Z = e^{N\beta J} \left[ \cosh \beta h + \sqrt{\sinh^2 \beta h + e^{-4\beta J}} \right]^N$$

$$+ \left[ \cosh \beta h - \sqrt{\sinh^2 \beta h + e^{-4\beta J}} \right]^N.$$  \hspace{1cm} (32)

The HF theorem gives access to the expectation values of either of the two terms in the Hamiltonian. Let us first calculate the thermal average of the interaction term, so that $H_1 \equiv H_J = -J \sum s_i s_j$. We define

$$H^{\lambda_1} = -J \lambda_1 \sum_{\langle i,j \rangle} s_i s_j - \lambda h \sum_i s_i,$$  \hspace{1cm} (33)

which leads to the partition function $Z^{\lambda_1}$:

$$Z^{\lambda_1} = e^{N\beta \lambda_1 J} \left[ \cosh \beta h + \sqrt{\sinh^2 \beta h + e^{-4\lambda_1 \beta J}} \right]^N$$

$$+ \left[ \cosh \beta h - \sqrt{\sinh^2 \beta h + e^{-4\lambda_1 \beta J}} \right]^N.$$  \hspace{1cm} (34)

The corresponding free energy is readily computed from $F^{\lambda_1} = -\frac{1}{\beta} \ln Z^{\lambda_1}$. With this, the thermal average of the interaction energy is given by

$$\langle H_J \rangle_T = \frac{\partial F^{\lambda_1}}{\partial \lambda_1} \bigg|_{\lambda_1=1}.$$  \hspace{1cm} (35)

The temperature dependence of $\langle H_J \rangle_T/N$, calculated according to the HF theorem, is reported in Fig. 2 (solid line). The calculations have been performed for couplings $J = 2$ and $h = 1$, and for $N = 10$ particles. At low temperatures, we find $\langle H_J \rangle_T/N \approx J$ as expected.

Alternatively, if we want to calculate the thermal average of the one-body interaction, $H_h = -\lambda \sum_i s_i$, we need to define,

$$H^{\lambda_2} = -J \sum_{\langle i,j \rangle} s_i s_j - \lambda \lambda_2 h \sum_i s_i,$$  \hspace{1cm} (36)

The corresponding partition function $Z^{\lambda_2}$ becomes

$$Z^{\lambda_2} = e^{N\beta \lambda_2 J} \left[ \cosh \beta \lambda_2 h + \sqrt{\sinh^2 \beta \lambda_2 h + e^{-4\lambda_2 \beta J}} \right]^N$$

$$+ \left[ \cosh \beta \lambda_2 h - \sqrt{\sinh^2 \beta \lambda_2 h + e^{-4\lambda_2 \beta J}} \right]^N.$$  \hspace{1cm} (37)

The thermal average of $H_h$ is then calculated as

$$\langle H_h \rangle_T = \frac{\partial F^{\lambda_2}}{\partial \lambda_2} \bigg|_{\lambda_2=1}.$$  \hspace{1cm} (38)

$\langle H_h \rangle_T/N$ is shown as a function of temperature in Fig. 2 (dashed line). As expected, as $T \rightarrow 0$, we find that $\langle H_h \rangle_T/N \rightarrow h$. In contrast, in the classical limit, the temperature washes out any residual magnetisation and $\langle H_h \rangle_T$ asymptotically tends to 0.
We also show in Fig. 2 the sum of the two terms in the Hamiltonian (dotted line). We compare this sum with an explicit calculation of the thermal average of the full Hamiltonian in Eq. (31) (circles). We find a perfect agreement within numerical errors. Notice that at zero temperature, the expectation value of the full Hamiltonian is \( \langle H \rangle_T / N = -(J + h) \). In other words, the \( H_J \) and \( H_h \) terms contribute to the total energy per particle in proportion to their respective couplings \( J \) and \( h \). In contrast, at very high temperatures, \( T \gg h \) and \( T \gg J \), the thermal average of the Hamiltonian decays with temperature, \( \langle H \rangle_T / N = -(J^2 + h^2)/T \). The two contributions now scale with \( J^2 \) and \( h^2 \). In the specific example shown in Fig. 2, the \( J \) term dominates at high temperatures by a factor of 4.

The HF theorem for the Ising model allows us to compute separately the thermal expectation values of \( H_J \) and \( H_h \). From a practical perspective, this provides an alternative way to compute the total energy of the system, with each level having an \( N \)-fold degeneracy. This model has been used in the context of nuclear physics and Glick to describe \( N \) fermions occupying two energy levels, with each level having an \( N \)-fold degeneracy.\(^{43,44} \) From a quantum mechanics teaching perspective, this example illustrates the use of creation and annihilation operators; the construction of Fock spaces; and the numerical diagonalization of a finite size Hamiltonian. We note that this model has also been explored at finite temperature in the past.\(^{38,45-47} \)

The last example will be devoted to a model proposed in the mid-60s of the last century by Lipkin, Meshkov and Glick to describe \( N \) fermions occupying two energy levels, with each level having an \( N \)-fold degeneracy.\(^{48} \) This model has been used in the context of nuclear physics and also as a laboratory to test many-body techniques.\(^{45} \)

From a quantum mechanics teaching perspective, this example illustrates the use of creation and annihilation operators; the construction of Fock spaces; and the numerical diagonalization of a finite size Hamiltonian. We note that this model has also been explored at finite temperature in the past.\(^{38,45-47} \)

The Hamiltonian\(^{48} \) of this model is typically made up of three terms:

\[
\hat{H} = \varepsilon \hat{J}_0 - \frac{V}{2} (\hat{J}_+^2 + \hat{J}_-^2) - \frac{W}{2} (\hat{J}_+ \hat{J}_- + \hat{J}_- \hat{J}_+) ,
\]

with

\[
\hat{J}_0 = \frac{1}{2} \sum_p \left[ \hat{a}_{p,1}^{\dagger} \hat{a}_{p,1} - \hat{a}_{p,-1}^{\dagger} \hat{a}_{p,-1} \right] ,
\]

\[
\hat{J}_+ = \sum_p \hat{a}_{p,1}^{\dagger} \hat{a}_{p,-1} , \quad \hat{J}_- = \sum_p \hat{a}_{p,-1}^{\dagger} \hat{a}_{p,1} ,
\]

where \( \hat{a}_{p,\pm 1}^{\dagger} \) and \( \hat{a}_{p,\pm 1} \) are the creation and annihilation operators on the top (+1) or bottom (−1) level in site \( p = 1, \cdots, N \). These operators satisfy the anti-commutation relations, \( \{ \hat{a}_{p,\alpha}, \hat{a}_{r,\beta}^{\dagger} \} = \delta_{p,r} \delta_{\alpha,\beta} \) and \( \{ \hat{a}_{p,\alpha}, \hat{a}_{r,\beta} \} = \{ \hat{a}_{p,\alpha}^{\dagger}, \hat{a}_{r,\beta}^{\dagger} \} = 0 \).

The first term in the Hamiltonian is associated to \( \hat{J}_0 \) and describes the system in absence of interactions. \( \varepsilon \) is the energy difference between the two levels, and is used as an energy unit in the reminder of this paper. The Fock states built with the creation operators diagonalize \( \hat{J}_0 \) and the total energy is proportional to the difference between the number of particles in the top and bottom levels. The dimension of this Fock space is \( 2^N \) as, in each of the \( N \) sites, particles can either be in the top or the bottom state, with one particle in each site. Any isolated two-level system is isomorphous to a spin−1/2 system, and so the operators \( \hat{J}_0, \hat{J}_+ \) and \( \hat{J}_- \) satisfy commutation relations that are characteristic of the algebra of angular momentum,

\[
[\hat{J}_+, \hat{J}_-] = 2\hat{J}_0 , \quad [\hat{J}_0, \hat{J}_+] = \hat{J}_+ , \quad [\hat{J}_0, \hat{J}_-] = -\hat{J}_- .
\]

One can then introduce the Casimir operator \( \hat{J}^2 = \frac{1}{2} (\hat{J}_+ \hat{J}_- + \hat{J}_- \hat{J}_+) + \hat{J}_0^2 \) and make use of the analogy with the angular momentum algebra to define the action of these operators on eigenvectors defined by the quantum numbers \( j \) and \( m, | j, m \rangle \),

\[
\hat{J}_0 \mid j, m \rangle = m \mid j, m \rangle ,
\]

\[
\hat{J}^2 \mid j, m \rangle = j(j+1) \mid j, m \rangle ,
\]

\[
\hat{J}_\pm \mid j, m \rangle = \sqrt{j(j+1) - m(m \pm 1)} \mid j, m \pm 1 \rangle .
\]

These eigenvectors are linear combinations of the Fock states constructed by acting with the creation operators on the vacuum. The matrix elements of the Hamiltonian are readily calculated using Eq. (42). For our purposes, \( i.e. \) to illustrate the fulfillment of the HF theorem, we neglect the contributions due to \( W \) and consider only the interaction term proportional to \( V \). There are only three non-zero combinations of matrix elements for a given value of \( j \),

\[
\langle j, m \mid \hat{H} \mid j, m + 2 \rangle = -\frac{V}{2} \sqrt{(j(j+1) - m(m+1))} \times \sqrt{(j(j+1) - (m+1)(m+2))} ,
\]

\[
\langle j, m \mid \hat{H} \mid j, m \rangle = \varepsilon \cdot m ,
\]

\[
\langle j, m + 2 \mid \hat{H} \mid j, m \rangle = \langle j, m \mid \hat{H} \mid j, m + 2 \rangle .
\]

At zero temperature, it is customary to set \( j = N/2 \), since the ground state of the system lies in the subspace with the maximum value of \( j \). \( m \) takes the values \( m = -j, -j+1, \cdots, j-1, j \), and for a given \( j \) this sets a subspace of dimension \( 2j+1 \). In a finite temperature setting, thermal fluctuations populate the states with \( j < \frac{N}{2} \). For an even (odd) number of particles \( N \), \( j \) can therefore take the values \( j = j_{\text{min}}, \cdots, N/2 \) with \( j_{\text{min}} = 0 \) (\( j_{\text{min}} = 1/2 \)).

The diagonalization of the Hamiltonian provides the eigenenergies of the different subspaces, \( E_k^{(j)} \), with \( k = 1, \cdots, 2j+1 \). The ground state is non degenerate, but
different subspaces with the same value of \( j \) generate the same eigenenergies. The multiplicity

\[
\alpha_j^N = \frac{1 + 2j}{1 + j} \frac{N}{2} - j, \quad (44)
\]

counts the number of times that an angular momentum \( j \) occurs for a given \( N \), i.e. the number of different SU(2) subspaces of dimension \( 2j + 1 \) arising from coupling \( N \) spins.\(^{45,46}\) Adding up the multiplicities of each subspace in \( j \), we recover the total dimension of the Fock space, \( \sum_j (2j + 1) \alpha_j^N = 2^N \).

We define the parametric Hamiltonian \( H^\lambda \) as

\[
\hat{H}^\lambda = \varepsilon \hat{J}_0 - \lambda \frac{V}{2} (\hat{J}_+^2 + \hat{J}_-^2), \quad (45)
\]

so that \( \hat{H}_1 = \frac{V}{T} (\hat{J}_+^2 + \hat{J}_-^2) \). After diagonalizing \( \hat{H}^\lambda \) in each of the \( j \)--subspaces, one obtains the eigenenergies \( E^{(j),\lambda}_k \) with \( k = 1, \ldots, 2j + 1 \). At finite temperature, the partition function is numerically calculated from the sum

\[
Z^\lambda = \sum_{j=\min}^{N/2} \alpha_j^N \sum_{k=1}^{2j+1} e^{-\beta E^{(j),\lambda}_k}. \quad (46)
\]

We can then calculate the energy, Eq. (9), and the free energy, \( F^\lambda = -T \ln Z^\lambda \). The thermal average of the interaction energy is then given by the HF theorem at finite temperature, Eq. (14). Alternatively, one can explicitly compute the expectation value of the interaction energy in each eigenstate, and perform the thermal average separately,

\[
(H_1)_T = \frac{1}{Z} \sum_{j=\min}^{N/2} \alpha_j^N \sum_{k=1}^{2j+1} \langle j, k | \hat{H}_1 | j, k \rangle e^{-\beta E^{(j),\lambda}_k}. \quad (47)
\]

The three panels in Fig. (3) provide an example of the results for the thermal Lipkin model. We choose \( N = 10 \) particles and \( V = 3 \) as an illustrative test. We report the total energy (solid line) and the free energy (dashed line) as a function of temperature in panel (a). Both \( E \) and \( F \) coincide at \( T = 0 \). As temperature increases, however, the energy is an increasing function of temperature. In contrast, the free energy decreases with temperature due to the contribution of the entropy.

The fulfillment of the HF theorem is illustrated in panel (b). We show \( \partial E^\lambda / \partial \lambda |_{\lambda=1} \) (solid line) and \( \partial F^\lambda / \partial \lambda |_{\lambda=1} \) (dotted line). The empty circles show the thermal average of the interaction term, \( \langle H_1 \rangle_T \). We stress that this average has been explicitly calculated using Eq. (47) rather than the derivative of \( F^\lambda \) with respect to \( \lambda \). We find a perfect agreement between these two independent calculations, thus providing a numerical proof of the generalization of the HF theorem to finite temperature. We note that for this example with \( V = 3 \), \( E \) in panel (a) and \( \langle H_1 \rangle_T \) in panel (b) are very similar.

The solid line in panel (b) corresponds to the energy derivative \( \partial E^\lambda / \partial \lambda |_{\lambda=1} \). The differences between the solid and dotted curves indicate the importance of the entropy contribution to the derivative of \( F^\lambda \) with respect to \( \lambda \). At low temperatures, \( T \lesssim 4 \), the differences between the derivatives of \( F^\lambda \) and \( E^\lambda \) are very small. At some point when increasing temperature, though, the energy
derivative shows a dip with a minimum around $T \approx 10$, and a subsequent increase with temperature. In contrast, the derivative of the free energy (and the thermal average of $\hat{H}_1$) are increasing functions of temperature throughout.

Finally, panel (c) of Fig. 3 shows the relation between the derivative of $S^\lambda$ with respect to $\lambda$ (solid line) and $\partial \langle \hat{H}_1 \rangle / \partial T$ (empty circles). This derivative is directly related to the slope of $\langle \hat{H}_1 \rangle_T$ as a function of temperature, shown in panel (b). At low temperatures, the temperature dependence of $\langle \hat{H}_1 \rangle_T$ is mild and the derivative is close to zero. At intermediate temperatures, the entropy derivative shows a maximum, in the same region where the energy derivative in panel (b) has a minimum. For $T \to \infty$, since the size of the Hilbert space we are considering is infinite, the system tends to equipartition, i.e., all states are equally populated. In particular, the entropy of the system in this limit is $S \to \ln 2^N$, and one expects it to be temperature (and $\lambda$) independent. Similar arguments hold for the energy and the free energy, so their derivatives saturate and cancel at (classically) high temperatures. The slow decrease of the derivative in panel (c) confirms numerically these expectations.

VI. SUMMARY AND CONCLUSIONS

The main purpose of this paper is to present a simple derivation of the Hellmann–Feynman theorem at finite temperature. Our aim is to illustrate its usefulness as a pedagogical tool in teaching quantum mechanics at finite temperature. We note that previous work on the subject has focused on specific research questions.

The theorem allows one to calculate the thermal average of operators contained in the Hamiltonian, by calculating the derivative of the free energy with respect to a parameter that modulates the action of operators in the Hamiltonian. The theorem is specially useful for cases where one has access to the free energy, but not necessarily to the separate expectation values of the individual terms in the Hamiltonian, like the kinetic and/or the interaction terms. We have also derived a relation between the variation of the entropy with respect to this parameter and the temperature derivative of the thermal average of the operator. This relation is not trivial a priori.

We have illustrated the usefulness of the HF theorem at finite temperature with three different examples that can be used in quantum mechanics or quantum statistical mechanics courses. Two of these examples, concerning the one-dimensional harmonic oscillator and the Ising model, are fully analytical and can be exploited in undergraduate courses. The third example, the Lipkin model, requires some knowledge of second quantization and the use of numerical diagonalization techniques, so it may be useful for more advanced, master-level courses.

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From now on, we explicitly display a hat, \( \hat{H} \), in the Hamiltonians to stress the fact that these are second-quantised operators.