Rayleigh-Ritz variational principle for ensembles of fractionally occupied states

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The Rayleigh-Ritz minimization principle is generalized to ensembles of unequally weighted states. Given the M lowest eigenvalues $E_1 \le E_2 \le \cdots \le E_M$ of a Hamiltonian H, and given M real numbers $w_1 \ge w_2 \ge \cdots \ge w_M > 0$, an upper bound for the weighted sum $w_1E_1 + w_2E_2 + \cdots + w_ME_M$ is established. Particular cases are the ground-state Rayleigh-Ritz principle ($M=1$) and the variational principle for equiensembles ($w_1 = w_2 = \cdots = w_M$). Applications of the generalized principle are discussed.

I. INTRODUCTION

The variational principle of Rayleigh and Ritz (RR) is one of the oldest and most powerful tools in quantum theory. Besides directly optimizing parametrized wave functions, the RR principle forms the basis of modern many-body techniques determining the best function in a class of trial wave functions (e.g., Slater determinants in Hartree-Fock theory). Another application is density-functional theory, the variational principle of Hohenberg and Kohn[1] being essentially a reformulation of the RR principle.

In most cases, the variational method is applied to the ground state. This is because, in applications to excited states, the trial wave functions must be orthogonal to all lower eigenstates. For the lowest eigenstates in a symmetry class, trial wave functions of that symmetry automatically satisfy this condition; for other eigenstates, however, ensuring orthogonality is prohibitively complicated. For excited states, therefore, the RR principle for equiensembles,[2] which provides upper bounds for the arithmetic average of the lowest M eigenvalues, constitutes an important alternative. Long ago applied[3] to the 2^1S term of He, this method more recently provided the foundation of Theophilou's density-functional formalism[4] for excited states.

In this paper, we shall derive a RR variational principle for more general ensembles, in which the lowest M eigenstates are weighted unequally. For noninteracting systems, these ensembles correspond to fractionally occupied single-particle states, a circumstance that motivated our study, as the following discussion explains.

That fractional occupation is convenient for calculating excitation energies was first pointed out by Slater.[5] On the basis of the Hartree-Fock-Slater theory,[6] he introduced the transition-state approach and derived an approximate expression relating the single-particle eigenvalues of the Hartree-Fock-Slater equations to the excitation spectrum. Following this development, Janak derived[7] an analogous relation in density-functional theory,[8] relating each Kohn-Sham[8] eigenvalue to the derivative of the total energy with respect to the occupation of the corresponding orbital. Although producing practical expressions for numerical applications,[9] these derivations are based on the ground-state formalism. Thus, for example, the transition-state approach[5] unwarrantedly assumes that the exchange potentials for the excited states and for the ground state have the same functional dependence on the density.

An alternative formulation, based on a Hohenberg-Kohn theorem and on Kohn-Sham equations for fractionally occupied states, seems therefore desirable. As shown in a subsequent paper,[10] hereafter named paper II, one such analysis, stemming from the RR principle for unequally weighted ensembles, leads to an exact expression relating the excitation energies to the Kohn-Sham eigenvalues. As usual in density-functional theory, an approximation is necessary to make this formal relation practical. The resulting, approximate expression is nonetheless significantly more accurate than Slater's formula;[5] this we show in a third paper,[11] hereafter named paper III, by computing the excitation spectrum for the He atom.

II. STATEMENT OF THE THEOREM

The generalized RR principle we want to establish applies to any time-independent Hamiltonian H, whose spectrum, generally degenerate, is given by

$$H|j\rangle = E_j|j\rangle \quad (j=1,2,3,\ldots)\ . \tag{1}$$

The eigenstates are numbered so that

$$E_1 \le E_2 \le E_3 \le \cdots\ . \tag{2}$$

Within each multiplet of degenerate energies, we choose an arbitrary set of orthonormal eigenstates and label them consecutively. Once chosen, the labeling is kept fixed in all further manipulations.

For any $m \le M$, $\mathcal{L}_m$ is defined as the subspace spanned by the eigenfunctions $|j\rangle$ of H with $E_j < E_m$. By $\mathcal{U}_m$ we denote the subspace spanned by the eigenfunctions $|j\rangle$ of H with $E_j \le E_m$, i.e., $\mathcal{U}_m$ comprises $\mathcal{L}_m$ and the complete multiplet of states with energy E_m (see Fig. 1).

After these preliminaries we can state the following theorem.

(a) Let $w_1, w_2, \ldots, w_M$ be real positive numbers ordered such that

$$w_1 \geq w_2 \geq \cdots \geq w_M > 0 \ . \tag{3}$$

Then the following inequality is satisfied for any set of orthonormal functions $\{|\phi_1\rangle, |\phi_2\rangle, \ldots, |\phi_M\rangle\}$:

$$w_1\langle\phi_1|H|\phi_1\rangle + \cdots + w_M\langle\phi_M|H|\phi_M\rangle \geq w_1E_1 + w_2E_2 + \cdots + w_ME_M \ . \tag{4}$$

(b) The equality in (4) holds if and only if for $m=M$, and for all other m with $w_m \neq w_{m+1}$, the subspace $[|\phi_1\rangle, |\phi_2\rangle, \ldots, |\phi_m\rangle]$ spanned by the trial functions $|\phi_1\rangle, |\phi_2\rangle, \ldots, |\phi_m\rangle$ lies in $\mathcal{U}_m$ and contains $\mathcal{L}_m$ as a subspace, i.e.,

$$\mathcal{L}_m \subset [|\phi_1\rangle, |\phi_2\rangle, \ldots, |\phi_m\rangle] \subset \mathcal{U}_m \ . \tag{5}$$

In terms of the labels r and s ($r+1 \leq m \leq s$) defined in Fig. 1, characterizing the multiplet of energies degenerate with E_m,

$$E_r < E_{r+1} = E_{r+2} = \cdots = E_m = \cdots = E_s < E_{s+1} \ , \tag{6}$$

the condition (5) can be stated alternatively as

$$[|1\rangle, |2\rangle, \ldots, |r\rangle] \subset [|\phi_1\rangle, |\phi_2\rangle, \ldots, |\phi_m\rangle] \subset [|1\rangle, |2\rangle, \ldots, |s\rangle] \ . \tag{7}$$

If an occupational jump, $w_m \neq w_{m+1}$, happens to coincide with a jump in the energy eigenvalues, $E_m \neq E_{m+1}$,

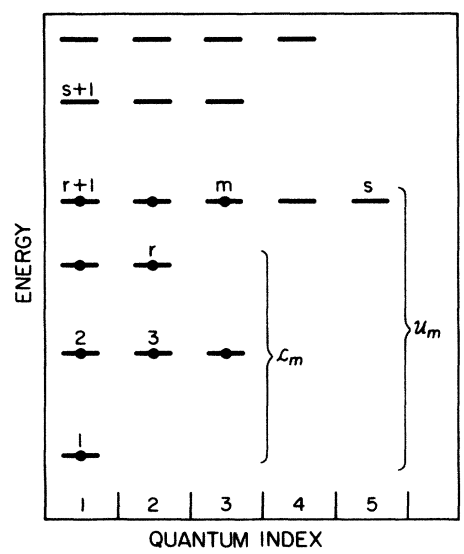

FIG. 1. The spectrum of the Hamiltonian H, Eq. (1), depicted schematically. The horizontal axis represents an index distinguishing between degenerate levels (e.g., the magnetic quantum number of orbitally degenerate atomic states). The vertical axis displays the energy. The solid circles identify the levels in the ensemble of the first m eigenstates. The curly brackets indicate the sets $\mathcal{L}_m \equiv [|1\rangle, |2\rangle, \ldots, |r\rangle]$ and $\mathcal{U}_m \equiv [|1\rangle, |2\rangle, \ldots, |s\rangle]$. As the relation (6) suggests, the mth state in the spectrum is generally degenerate, and in general the highest multiplet (i.e., the multiplet $|r+1\rangle, |r+2\rangle, \ldots, |m\rangle, \ldots, |s\rangle$) in that ensemble is partially occupied.

the second relation in (7) yields $[|\phi_1\rangle, |\phi_2\rangle, \ldots, |\phi_m\rangle] \subset [|1\rangle, |2\rangle, \ldots, |m\rangle]$. Since $|\phi_1\rangle, |\phi_2\rangle, \ldots, |\phi_m\rangle$ are orthonormal, the two subspaces $[|\phi_1\rangle, |\phi_2\rangle, \ldots, |\phi_m\rangle]$ and $[|1\rangle, |2\rangle, \ldots, |m\rangle]$ have the same (finite) dimension and are therefore identical. In that case,

$$[|1\rangle, |2\rangle, \ldots, |r\rangle] \subset [|\phi_1\rangle, \phi_2\rangle, \ldots, |\phi_m\rangle]$$

is automatically satisfied, so that the relations (5) or (7), respectively, take the simple form

$$[|\phi_1\rangle, |\phi_2\rangle, \ldots, |\phi_m\rangle] = [|1\rangle, |2\rangle, \ldots, |m\rangle] \ . \tag{8}$$

To illustrate part (b) of the theorem, we consider the case $M=2$ for a nondegenerate ground state $|1\rangle$ and a possibly degenerate first excited state $|2\rangle$, i.e.,

$$E_1 < E_2 = \cdots = E_p < E_{p+1}, \quad p \geq 2 \ . \tag{9}$$

If the states are equally weighted, $w_1 = w_2$, the relation (7) needs to be satisfied only for $m=2$, i.e.,

$$|1\rangle \in [|\phi_1\rangle, |\phi_2\rangle] \subset [|1\rangle, |2\rangle, \ldots, |p\rangle] \ . \tag{10}$$

In other words, the equality in (4) holds if and only if the trial states $|\phi_1\rangle, |\phi_2\rangle$ are chosen from the subspace $[|1\rangle, |2\rangle, \ldots, |p\rangle]$ in such a way that $|1\rangle$ is contained in $[|\phi_1\rangle, |\phi_2\rangle]$. The situation is particularly simple if E_2 is nondegenerate ($p=2$). In this case, the subspaces $[|\phi_1\rangle, |\phi_2\rangle]$ and $[|1\rangle, |2\rangle]$ are identical, so that $|1\rangle \in [|\phi_1\rangle, |\phi_2\rangle]$ is redundant. Therefore, the condition (10) takes the form

$$[|\phi_1\rangle, |\phi_2\rangle] = [|1\rangle, |2\rangle] \ . \tag{11}$$

On the other hand, if $w_1 \neq w_2$, the relation (7) must hold, in addition, for $m=1$. This yields $[|\phi_1\rangle] \subset [|1\rangle]$, saying that

$$|\phi_1\rangle = |1\rangle \ . \tag{12}$$

The first part of relation (10), $|1\rangle \in [|\phi_1\rangle, |\phi_2\rangle]$, is then automatically satisfied. Thus, for $w_1 \neq w_2$, the equality in (4) holds if and only if

$$|\phi_1\rangle = |1\rangle \quad \text{and} \quad |\phi_2\rangle \in [|2\rangle, |3\rangle, \ldots, |p\rangle] \ . \tag{13}$$

Once again, the situation is particularly simple if E_2 is nondegenerate. In that case,

$$|\phi_1\rangle = |1\rangle \quad \text{and} \quad |\phi_2\rangle = |2\rangle \tag{14}$$

is necessary and sufficient for the equality in (4) to hold.

The two-state example suggests that part (b) of the theorem can be cast into a simpler form if all states included in the ensemble are nondegenerate, or, more generally, if the occupation numbers remain constant within each multiplet of degenerate energies. A *block* of indices $\{l, l+1, \ldots, l+t\}$ characterized by constant occupation numbers $w_{l-1} \neq w_l = w_{l+1} = \cdots w_{l+t} \neq w_{l+t+1}$ then comprises a complete multiplet or a set of complete multiplets with successive energies. Since, in this case, all occupational jumps, $w_m \neq w_{m+1}$, coincide with jumps of the energy, $E_m \neq E_{m+1}$, the condition (5) always takes the form of Eq. (8). As an immediate consequence of the required orthonormality of the trial functions, the equality

in (4) then holds if and only if for each block $\{l, l+1, \ldots, l+t\}$ with $w_{l-1} \neq w_l = \cdots = w_{l+t} \neq w_{l+t+1}$ the trial states $|\phi_l\rangle, |\phi_{l+1}\rangle, \ldots, |\phi_{l+t}\rangle$ lie in the subspace spanned by the eigenstates $|l\rangle, |l+1\rangle, \ldots, |l+t\rangle$, i.e.,

$$[|\phi_l\rangle, |\phi_{l+1}, \ldots, |\phi_{l+t}\rangle] = [|l\rangle, |l+1\rangle, \ldots, |l+t\rangle] . \quad (15)$$

III. PROOF OF THE THEOREM

To prove the theorem, one has to demonstrate that the quantity

$$(\Delta E)_M = \sum_{m=1}^{M} w_m [\langle \phi_m | H | \phi_m \rangle - E_m] \quad (16)$$

is non-negative [part (a)], and vanishes if and only if the condition $\mathcal{L}_m \subset [|\phi_1\rangle, |\phi_2\rangle, \ldots, |\phi_m\rangle] \subset \mathcal{U}_m$ holds for $m = M$ and for all other m with $w_m \neq w_{m+1}$ [part (b)]. For notational convenience, we define

$$w_{M+1} \equiv 0 . \quad (17)$$

This allows us to rewrite Eq. (16) as

$$(\Delta E)_M = \sum_{m=1}^{M} (w_m - w_{m+1}) \sum_{k=1}^{m} [\langle \phi_k | H | \phi_k \rangle - E_k] . \quad (18)$$

For an equiensemble of m states, i.e., for the particular set of occupation numbers $w_1 = w_2 = \cdots = w_m = 1$, $w_{j>m} = 0$, the quantity defined by Eq. (16) becomes

$$(\Delta E)_m^{\text{equi}} = \sum_{k=1}^{m} [\langle \phi_k | H | \phi_k \rangle - E_k] . \quad (19)$$

Equation (18) therefore enables us to treat the general ensemble of unequally weighted states as a linear superposition of equiensembles

$$(\Delta E)_M = \sum_{m=1}^{M} (w_m - w_{m+1}) (\Delta E)_m^{\text{equi}} . \quad (20)$$

Since, by construction, $w_m \geq w_{m+1}$, it only remains to be shown that $(\Delta E)_m^{\text{equi}} \geq 0$. To this end, we expand the trial functions $|\phi_k\rangle$ in the complete set of eigenfunctions of H,

$$|\phi_k\rangle = \sum_{j=1}^{\infty} \alpha_{kj} |j\rangle \quad (k = 1, 2, \ldots, M) , \quad (21)$$

the coefficients obeying the normalization condition

$$\sum_{j=1}^{\infty} |\alpha_{kj}|^2 = 1 \quad (k = 1, 2, \ldots, M) . \quad (22)$$

Being orthonormal, the set $\{|\phi_1\rangle, |\phi_2\rangle, \ldots, |\phi_M\rangle\}$ can be complemented by appropriately chosen states $|\phi_{M+1}\rangle, |\phi_{M+2}\rangle, \ldots$ to form a complete, orthonormal basis. Expanding the eigenstates of H in this basis we find

$$|j\rangle = \sum_{k=1}^{\infty} \alpha_{kj}^* |\phi_k\rangle \quad (j = 1, 2, \ldots) ; \quad (23)$$

consequently,

$$\sum_{k=1}^{\infty} |\alpha_{kj}|^2 = 1 \quad (j = 1, 2, \ldots) . \quad (24)$$

Substituting Eq. (21) for $|\phi_k\rangle$ on the right-hand side of Eq. (19) we find

$$(\Delta E)_m^{\text{equi}} = \sum_{j=1}^{\infty} p_j E_j - \sum_{j=1}^{m} E_j , \quad (25)$$

where

$$p_j = \sum_{k=1}^{m} |\alpha_{kj}|^2 \quad (26)$$

denotes the probability that the eigenstate $|j\rangle$ lie in the subspace $[|\phi_1\rangle, |\phi_2\rangle, \ldots, |\phi_m\rangle]$. Clearly,

$$0 \leq p_j \leq 1 \quad (27)$$

and

$$\sum_{j=1}^{\infty} p_j = m . \quad (28)$$

Equation (25) can be written

$$(\Delta E)_m^{\text{equi}} = \sum_{j=1}^{m} (p_j - 1) E_j + \sum_{j=m+1}^{\infty} p_j E_j , \quad (29)$$

from which we deduce that

$$(\Delta E)_m^{\text{equi}} = \sum_{j=1}^{m} (1 - p_j)(E_m - E_j) + \sum_{j=m+1}^{\infty} p_j (E_j - E_m) . \quad (30)$$

In view of the inequality (27), each term on the right-hand side of Eq. (30) is non-negative, i.e., $(\Delta E)_m^{\text{equi}} \geq 0$, which proves part (a) of the theorem.

To prove part (b), we refer to Fig. 1. The degeneracy associated with E_m reduces Eq. (30) to the form

$$(\Delta E)_m^{\text{equi}} = \sum_{j=1}^{r} (1 - p_j)(E_m - E_j) + \sum_{j=s+1}^{\infty} p_j (E_j - E_m) . \quad (31)$$

This expression vanishes if and only if $p_j = 1$ for $j \leq r$ and $p_j = 0$ for $j > s$, which means that

$$\mathcal{L}_m \subset [|\phi_1\rangle, |\phi_2\rangle, \ldots, |\phi_m\rangle] \subset \mathcal{U}_m . \quad (32)$$

Thus, $(\Delta E)_M$ vanishes if and only if (32) is satisfied for all m such that $w_m \neq w_{m+1}$, which completes the proof of part (b).

IV. CONCLUDING REMARKS

To close our discussion of the RR principle for unequally weighted ensembles, a brief comparison with the long established[2] equiensemble principle seems appropriate. The latter is a particular case of the former, all the w_j in Eq. (4) taking the same value, $w = w_1 = \cdots = w_M > 0$. Since the choice of w is immaterial, changes in w being equivalent to changes in the

unit of energy, the number of trial states (M) determines the entire ensemble. In contrast, for fixed M, the inequalities in (3) allow us to vary continuously the difference between the weights attributed to any two states. This adds flexibility to the variational method. The central result of paper II, an exact relation between excited energies and Kohn-Sham eigenvalues, is an example of how this flexibility can be exploited.

We finally note that the relation (4) is valid also for infinite ensembles,

$$\sum_{m=1}^{\infty} w_m \langle \phi_m \mid H \mid \phi_m \rangle \geq \sum_{m=1}^{\infty} w_m E_m \ , \tag{33}$$

provided $\sum_{m=1}^{\infty} w_m E_m$ is convergent. The relation (33) holds for arbitrary orthonormal systems $\mid \phi_m \rangle$ ($m = 1, 2, 3, \ldots$); the left-hand side, however, may be plus infinity.

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