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BRIEF COMMUNICATION

Restrictions on second order response properties of quantum states

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Abstract We distinguish two extreme classes of perturbation problems depending on the signs of second-order response properties. The first class refers to a positive value of the same for any state, and is overwhelmingly more probable. The other category offers all-but-one negative values, or at least some negative values for highly excited states. The classes are seen to differ in reproducing results of finite-dimensional matrix Hamiltonian perturbations, allowing the emergence of a type of sum rule. A few analytical findings are employed for direct demonstration. The outcomes provide notable restrictions on second order response properties of quantum states.

Keywords Perturbation theory · Second-order energy correction · Response properties · Sum rules

1 Introduction

In presence of an external perturbation λV, energy eigenvalues E_{n0} of a system, defined by the Hamiltonian H_0, are modified. The eigenenergy $E_n$of $H = H_0 + \lambda V$ is given by a power series in λ as

$$E_n = E_{n0} + \lambda E_{n1} + \lambda^2 E_{n2} + \cdots . \tag{1}$$

Conventionally, perturbation problems [1–3] are distinguished on the basis of convergence or divergence of (1). Thus, one separates regular perturbations from singular ones [3]. However, it is true that the leading nontrivial effect of the external perturbation is contained in the second order correction factor E_{n2} in (1). Accordingly, the

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second-order response property is given by

$$\alpha_n = -\lim_{\lambda \to 0} \left(\frac{d^2 E_n}{d\lambda^2} \right) = -2E_{n2}. \tag{2}$$

Thus, studies on properties of α_n become important. Polarizability and susceptibility are the two most significant examples of this kind of response in atomic and molecular domains. We shall see how the nature of α_n alone can classify perturbation problems in a different way.

It is well known in non-degenerate Rayleigh-Schrödinger perturbation theory (RSPT) [1–3] that the second-order energy correction term has the form

$$E_{n2} = \sum_{m \neq n}^{\infty} \frac{|V_{mn}|^2}{E_{n0} - E_{m0}} = \sum_{m=0}^{n-1} \frac{|V_{mn}|^2}{E_{n0} - E_{m0}} + \sum_{m=n+1}^{\infty} \frac{|V_{mn}|^2}{E_{n0} - E_{m0}} \tag{3}$$

where $V_{mn} = \langle \Psi_{m0} | V | \Psi_{n0} \rangle$. Therefore, one immediately notes that

$$E_{02} < 0; \;\; \alpha_0 > 0. \tag{4}$$

So, a definite conclusion about the sign of α follows for the *ground state only* ($n = 0$). In (3), however, the first part of the sum provides a positive contribution. But, one is never sure whether this part will dominate the overall behavior for some n-th state, in general. Hence, property $\alpha_n (n > 0)$ will not have any *specific* sign that is universal, independent of the *nature* of the problem. Therefore, it will be worthwhile to look for generalities like when *all* $\alpha_n (n > 0)$ will have a *definite* sign, either positive or negative, and, if so, how probable are these two extreme varieties. It is important to gather some such information because this quantity determines the *primary response* of the unperturbed system for a given perturbation in the concerned quantum state.

Employing (3), we obtain an interesting inequality [2]

$$\sum_{n=0}^{K} E_{n2} < 0, \tag{5}$$

for any $K \geq 0$. This is easy to verify, but (5) does not seem to have attracted much attention. In case of finite-dimensional $[(N+1)]$ matrix perturbation problems, the inequality in (5) would hold for any $K < N$; only for $K = N$ we have the *equality*

$$\sum_{n=0}^{N} E_{n2} = 0. \tag{6}$$

Therefore, it may be taken generally for granted that, in case of quantum-mechanical problems, where $N \to \infty$, we would have the *inequality* in (5) valid for *any* K. Strangely, however, we shall notice that *a class* of Hilbert space problems does satisfy (6), *contrary* to traditional wisdom [4].

Specifically, the present investigation reveals that (i) it is much more probable to obtain a *positive* second-order response for any state and (ii) if $\alpha_n (n > 0)$ turns out to be *negative*, *at least for large n*, the equality in (6) is satisfied. The results can be summarized in the following forms

$$\alpha_n > 0, \text{ all } n : \Rightarrow \sum_{n=0}^{\infty} \alpha_n > 0; \tag{7}$$

$$\alpha_0 > 0; \ \alpha_n < 0, \ n \neq 0 : \Rightarrow \sum_{n=0}^{\infty} \alpha_n = 0. \tag{8}$$

$$\alpha_0 > 0; \ \alpha_n < 0, \ \text{large } n : \Rightarrow \sum_{n=0}^{\infty} \alpha_n = 0. \tag{9}$$

Note that the second part is obvious in (7) from the first part, but the same is not true of (8) or (9). Hence, one can have $\alpha_n < 0$ starting from $n = 1$ onwards, as in (8), or even can have arbitrary signs over low to moderate range of n, as in (9), and yet the second part in (8) or (9) would be valid in the same manner. Thus, the summation part additionally offers a nice sum rule for a class of problems.

A few other features are worth mentioning. First, the signs of $\{E_{n2}\}$ cannot vary arbitrarily because they have to satisfy (3). However, the chance of finding a positive $E_{n2}(i.e., \alpha_n < 0)$ apparently increases with increasing n due to the involvement of a larger number of positive terms in the sum (3). Second, cases where E_{n2} can be obtained in closed forms provide some insight into potential families that always yield a second-order shift of a definite sign for any state. Indeed, here lies the motivation behind studies on simple systems that offer exact analytic results for E_{n2}. Third, we find it coincidentally that the agreement between finite $[(N+1)]$ and infinite $[N \to \infty]$ dimensional results regarding the equality in (4) occurs only when we have a set of *all positive*E_{n2}, at least for large n. Such an outcome can be generally proved and, in situations, are verifiable with model potentials. The final conclusions are independent of dimension and particle number, however.

2 The main results

Denoting E_{02} by $-\varepsilon(\varepsilon > 0)$, we obtain from (5), for $K = 1$,

$$E_{12} < \varepsilon. \tag{10}$$

More specifically, (10) can be written as

$$E_{12} = \beta_1 \varepsilon, \ \beta_1 < 1. \tag{11}$$

For $K = 2$ in (5), one can likewise write

$$E_{22} = \beta_2 (1 - \beta_1) \varepsilon, \ \beta_2 < 1. \tag{12}$$

In general, therefore, it follows that

$$E_{k2} = \beta_k(1-\beta_{k-1})\ldots(1-\beta_1)\varepsilon,\ \ \beta_k < 1, \tag{13}$$

where the preceding equations define the earlier β_j. Form (13) is a kind of hierarchical relationship. It provides the key to understanding and arriving at our major conclusions, as may be witnessed below:

I. We first cast our problem in the following way. Suppose *all* E_{k2} terms ($k > 0$) are positive or zero. This implies, β_k is bounded by $0 \le \beta_k < 1$. In such a situation, one can also order E_{n2} as

$$|E_{02}| > E_{12} > E_{22} > E_{32}\cdots \quad . \tag{14}$$

On the other hand, if *all* E_{k2} terms ($k > 0$) are negative semidefinite, β_k will satisfy $-\infty < \beta_k \le 0$. The domains of $\{\beta_j\}$ [respectively unity (finite) and infinite] immediately point to the *overwhelmingly* larger probability of encountering the latter situation than the former, for arbitrary perturbations on arbitrary states. Thus, condition (7) on any second order property is the *most probable* candidate for observations.

II. One may next appreciate why the equality (6) will be valid even for infinite-dimensional cases, provided, of course, that *all* E_{k2} terms for excited states are *positive semidefinite* (this point may further be relaxed, see point IV below). Indeed, we can choose here, without any loss of generality,

$$\beta_k = \sin^2\theta_k,\ \ 0 \le \theta_k < \pi/2. \tag{15}$$

Then, it is easy to show that the left side of (6) takes the form

$$\sum_{k=0}^{K} E_{k2} = -\,\varepsilon\prod_{k=1}^{K}\cos^2\theta_k. \tag{16}$$

But, for arbitrary $\{\theta_k\}$, the right hand part of (16) tends to zero as $K \to \infty$. Thus, for such a class of infinite-dimensional problems, it is *natural* that the *equality* in (6) will be obeyed, though (6) is originally a finite-dimensional result. This corresponds to case (8).

III. The other possibility, on the contrary, is wide open. For example, if we choose $\{E_{k2}\}$ as *negative semidefinite* and similarly bounded (*i.e.*, $-\infty < \beta_k \le 0$), it is permissible to take, instead of (15),

$$\beta_k = -\tan^2\theta_k,\ \ 0 \le \theta_k < \pi/2. \tag{17}$$

As a result, we are led to a sum of all negative terms

$$\sum_{k=0}^{\infty} E_{k2} = -\,\varepsilon\prod_{k=1}^{\infty}\sec^2\theta_k,\ \ \ 0 \le \theta_k < \pi/2. \tag{18}$$

One sees that, while a product term similar to (16) appears at (18), it now increases without limit for arbitrary $\{\theta_k\}$, *i.e*., arbitrary perturbations, and hence the *inequality* in (5) will *always* hold. Indeed, the right side of (18) becomes infinite in magnitude. As already mentioned in I, such cases are likely to show up under general conditions, and they all refer to criterion (7) for a second-order property.

IV. Finally, we plan to choose the case of mixed signs. From (3), we already noticed that, for large n, the chance of finding a positive E_{n2} *cannot* decrease with increasing n because of the involvement of a larger number of positive terms. So, in order to deal with a very general but *systematic* situation, one may take, for example, that the first $(J+1)$ terms are negative, and the subsequent ones are all positive. Then, of course, we obtain a result by combining (15) and (17) in the form

$$\begin{aligned}\sum_{k=0}^{\infty} E_{k2} &= -\varepsilon \prod_{k=1}^{J} \sec^2\theta_k \prod_{k=J+1}^{\infty} \cos^2\theta_k, \quad 0 \leq \theta_k < \pi/2 \\ &= 0. \end{aligned} \tag{19}$$

The last result has its underlying reason same as the one appeared below (16). The case of *random* mixed signs for the first $(J+1)$ terms leads similarly to

$$\begin{aligned}\sum_{k=0}^{\infty} E_{k2} &= -\varepsilon \prod_{i,l=1\ (l\neq i)}^{J} \left(\sec^2\theta_i \ \cos^2\theta_l\right) \prod_{k=J+1}^{\infty} \cos^2\theta_k, \quad 0 \leq \theta_k < \pi/2 \\ &= 0. \end{aligned} \tag{20}$$

Therefore, here too, the finite-dimensional outcome is revealed. Hence, it is now transparent that one can get *a class of problems* for which results of finite and infinite dimensions agree under conditions less restrictive than those involved in (15). Indeed, this corroborates with our remark (9) on the properties of α_n.

All the above results are general ones in the sense that they do not depend on the dimensionality (or, particle number) of the problem. They are also independent of the level of approximation of a practical theory that leads to (1).

3 Demonstrative case-studies

The primary motivation behind such a study has emerged out of a curious observation on a large number of model Hamiltonians for which exact E_{n2} are calculable. For example, RSPT studies [5–7] on the harmonic oscillator show that the Hamiltonian

$$H = -\frac{1}{2}\frac{d^2}{dx^2} + x^2 + \lambda x^M. \tag{21}$$

yields the feature $E_{n2} < 0$ for *any* M and at *any* n. Here are a few results of E_{n2} *at large* n where one normally expects otherwise:

$$M = 3: \ -\frac{7}{4}n^2; \quad M = 4: \ -\frac{17}{4}n^3;$$
$$M = 5: \ -\frac{187}{16}n^4; \quad M = 6: \ -\frac{393}{16}n^5. \tag{22}$$

The trend is clear; with increasing M, E_{n2} tends to be more negative. Likewise, results [7,8] for the hydrogenic s-state Hamiltonian of the form

$$H = -\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{1}{r} + \lambda r^M \tag{23}$$

leads again to similar trends of E_{n2} for *any* M. In the large-n limit, one finds that

$$M = 1: -\frac{7}{8}n^6; \ M = 2: -\frac{143}{16}n^{10};$$
$$M = 3: -\frac{7365}{128}n^{14}; \ M = 4: -\frac{80123}{256}n^{18}. \tag{24}$$

Once more, let us notice that $E_{n2} < 0$ for *any* n and at *any* M. It is also seen from (22) and (24) that E_{n2} will only be more negative for larger M. Since the harmonic oscillator and H atom problems are two primary exactly-solvable problems in quantum mechanics, and perturbations of the form (21) or (23) constitute an infinitude of possibilities, one is inclined to believe that some kind of generality should involve the observation $E_{n2} < 0$ ($n > 0$). The only exception, to the best of our knowledge, is the particle-in-a-box (PB) perturbed by a specific (linear) perturbation [9–11]. It has, therefore, attracted our attention to provide a general proof of the *prominence* of $E_{n2} < 0$ under general circumstances, implying case (7), as we showed.

Since we choose a very general, statistical approach, our main results have little to do with analytically solvable problems; however, a few other findings do have their roots in exactly obtainable corrections. They would serve as examples of the assertion (8) or (9), depending on the situation.

To proceed, we choose a few examples of sinusoidal perturbations of the PB problem ($m = 1/2, \hbar = 1$) in (0, 1). Standard RSPT outcome with the perturbation $\cos(\pi x)$ is the following:

$$E_{12} = -\frac{1}{12\pi^2}, \quad E_{k2} = \frac{1}{4\pi^2}\left(\frac{1}{2k-1} - \frac{1}{2k+1}\right), \ k > 1. \tag{25}$$

The required sum for the left side of (5) gives

$$\sum_{k=1}^{\infty} E_{k2} = \frac{1}{4\pi^2}\left[-\frac{1}{3} + \left(\frac{1}{3} - \frac{1}{5}\right) + \left(\frac{1}{5} - \frac{1}{7}\right) + \cdots\right]$$
$$= 0. \tag{26}$$

Therefore, it stands as a concrete example of (8).

We now choose the perturbation $\cos(2\pi x)$. This will partly justify (9). One may check that the results are

$$E_{12} = \frac{1}{4\pi^2(1^2 - 3^2)},\ E_{22} = \frac{1}{4\pi^2(2^2 - 4^2)},\ E_{k2} = \frac{1}{8\pi^2}\left(\frac{1}{k^2 - 1}\right), k > 2. \quad (27)$$

It follows immediately from (27) that

$$\sum_{k=1}^{\infty} E_{k2} = 0. \quad (28)$$

In fact, even if the *first few* E_{k2} are negative or have *random* signs, but subsequent ones are *all positive*, a characteristic feature like (9) can be easily found. For example, consider next the perturbations $\cos(3\,\pi x)$ and $\cos(4\pi x)$ of the PB. The results here are interesting and provide full justification of (9). We have found that in the former case $E_{12} < 0$, $E_{22} > 0$, $E_{32} < 0$, but $E_{j2} (j \geq 4)$ terms are all positive. The sum, however, satisfies (28). Similarly, effect of $\cos(4\,\pi x)$ is to furnish $E_{12} < 0$, $E_{22} < 0$, $E_{32} > 0$, $E_{42} < 0$ and $E_{j2}(j \geq 5) > 0$, but (28) is obeyed again. Indeed, these sinusoidal perturbations reveal a few remarkable facets in the current context. Thus, one can get *a class of problems* for which results of finite and infinite dimensions agree under conditions less restrictive [e.g., (20)] than those involved in (15) and hence obeys (9).

It is rather appealing to see, a posteriori, why most one–dimensional perturbation problems that are analytically solvable yield *all negative* second order corrections. In fact, both the harmonic oscillator and H-atom perturbations [see (5) and (7)] are such that the n-dependence of energy would only be larger. A pure oscillator shows a linear dependence with n. But, the effect of the total potential is such that the corrections would only increase the power of n. In case of the PB, however, the maximum dependence already exists ($n = 2$). So, either this will prevail, or it can only decrease. Hence, the corrections cannot show an unbounded increase with n. This is clear in all the examples with the PB. We observe that $E_{n2} \sim 1/n^2$. In other words, the large-n behavior of the corrections, if they depend on positive powers of n, can only be negative to satisfy (5).

One can now also explain qualitatively why polarizability of H atom in any state [12–14] would be positive, if we remember that the quantity is proportional to volume, (*i.e.*, r^3) and r goes as n^2. A similar conclusion follows for susceptibility that varies as the area (*i.e.*, r^2). In both these cases [15], second order energy corrections are therefore likely to be negative for any state.

4 Conclusion

In fine, we have justified that there are two extreme classes of perturbation problems. The statistically more probable first class refers to situations with all $E_{k2} < 0$ and inequality (5) is obeyed by them in the $K \to \infty$ limit. For the other class, we have all $E_{k2} > 0$, except for the ground state, and equality (6) is satisfied. The last result is also true of cases where the first few E_{k2} may have arbitrary signs, but subsequent ones are all positive. While the first class of problems (case III) possesses an immediate practical appeal in respect of response properties [16], the second class (case II), along with a subclass of problems (case IV) is theoretically more fascinating because of the satisfaction of (6), which is typical of finite-dimensional matrix perturbations, and normally one does not expect [4] infinite-dimensional problems to show up characteristics of finite-dimensional ones. We note how such results put restrictions (7)–(9) on response properties in an important way and yield sum rules in cases (8) and (9). The hierarchical relationship (13) for any second-order property translates as

$$\alpha_1 = -\beta_1\alpha_0,\ \ \beta_1 < 1,$$
$$\alpha_k = -\beta_k(1-\beta_{k-1})\ldots(1-\beta_1)\alpha_0,\ \ \beta_k < 1.$$

Such inequalities among the properties $\{\alpha_n\}$ of different quantum states may serve as useful checks in approximate computations at various levels. Particularly for excited states, it is known that contribution of the continuum is negligible in polarizability calculations [17]. Therefore, the above chain rule will be more significant for larger k. The link with ionization energy [18] may also turn out to be rewarding. A few model problems demonstrate our assertions nicely. It will be of interest to notice how far practical problems benefit from these observations.

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