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On the sign of the second-order energy shift in the Rayleigh–Schrödinger perturbation theory for a highly excited state

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Abstract
The second-order energy shift in the Rayleigh–Schrödinger perturbation theory is most likely to be positive for large quantum numbers, i.e. for excited states. Within the Wilson–Sommerfeld approximation, good for large quantum numbers, we show on the contrary that the sufficient condition for the second-order shift to be negative is, that the total potential be symmetric and both the unperturbed and perturbed potentials be monotonically increasing.

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1. Introduction

Perturbation theory [1–10] is a common tool in the study of eigenvalue problems. A classic case of an eigenvalue problem is the time-independent Schrödinger equation, which can be written as

$$H\psi = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \tag{1.1}$$

where H is called the Hamiltonian, m is the mass of the particle whose wavefunctions are given by $\psi(\vec{r})$ and whose eigenenergy is E. The problem is to find the allowed energies E_n and the corresponding wavefunctions ψ_n. The energies E_n are generally discrete and forced by boundary conditions of the problem. There are very few situations where E and ψ can be exactly determined. The shape-invariant potentials for which exact solutions can be found are discussed in [11]. If we denote the Hamiltonian for which an exact solution can be found by H_0, then an arbitrary Hamiltonian H can be written as

$$H = H_0 + \lambda H' \tag{1.2}$$

where λ is a parameter and H' is called the perturbing Hamiltonian. In this case, if the eigenvalue of H_0 is denoted by $E_n^{(0)}$ and the eigenfunctions by $\psi_n^{(0)}$ then the eigenvalues E_n of H can be written in a power series expansion as

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots, \tag{1.3}$$

with

$$E_n^{(1)} = \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle, \tag{1.4}$$

$$E_n^{(2)} = \sum_{l \neq n} \frac{|\langle \psi_n^{(0)} | H' | \psi_l^{(0)} \rangle|^2}{E_n^{(0)} - E_l^{(0)}}, \tag{1.5}$$

and so on. The classic textbooks and reviews [1–7] concentrated mainly on the applicability and methodology of perturbation theory. Complex problems in this domain include (i) adequacy of the decomposition equation (1.2), (ii) summability of equation (1.3) and (iii) cases where the unperturbed and perturbed spectra do not possess a one-to-one mapping. A number of more recent works appeared to overcome varying types of specific problems. For example, the calculation of $E_n^{(m)}$ using functions that are not quadratically integrable has been considered [8]. A perturbation theory using Kolmogorov's averaging method has been put forward [9]. Certain numerical instabilities have been noted and a way to handle these instabilities in the Rayleigh–Schrödinger perturbation theory has also been provided [10].

It is, however, true that in spite of all such studies, little is known about the general properties of $E_n^{(m)}$. One knows only that

(i) $E_n^{(1)} > 0$ for a positive definite H', and vice versa,
(ii) $E_0^{(2)} < 0$ for any perturbation, and
(iii) $E_0 \leqslant E_0^{(0)} + \lambda E_0^{(1)}$, a variational result.

We may, nevertheless, ask a few more pertinent questions: If $E_n^{(2)} < 0$, when does it follow that $E_{n+1}^{(2)} < 0$? Is there any valid ordering of the type $E_n^{(2)} < E_{n+1}^{(2)}$, or the reverse, and, if so, when? Are there cases for which all $E_n^{(2)} < 0$ follow, and, if so, under what condition? None of these questions seem to have any answer in the literature. What is more, such questions have never been asked either.

In this work, we shall pay attention to the last question of the previous paragraph: when does $E_n^{(2)} < 0$ follow? The first motivation is provided by several perturbative examples from two well-known and exactly solvable H_0, namely the harmonic oscillator and the hydrogen atom. Indeed, we shall presently see that there exists an infinitude of cases where $E_n^{(2)} < 0$ is valid, though no proof is available. Secondly, the observation generates two classes of potentials, one of which yields a negative second-order response to energy for any state. For atomic systems, one such important response property is the polarizability. Therefore, one may be tempted to ask the opposite question 'can the polarizability be negative for any nondegenerate state?' A precise answer to such a question seems demanding. More generally, one may be interested to gain insight into potential families that always yield a positive (or negative) second-order response for any state.

As regards the observations, we begin with the perturbation series for the one-dimensional harmonic oscillator

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 + \lambda x^{2\nu}, \tag{1.6}$$

which has been well studied for several values of ν by Reid [12] and Swenson and Danforth [13]. The results for the nth energy level are as follows

$$\nu = 2, \quad E_n^{(2)} = -\left(\tfrac{21}{8} + \tfrac{59}{8}n + \tfrac{51}{8}n^2 + \tfrac{17}{4}n^3\right); \tag{1.7}$$

$$\nu = 3, \quad E_n^{(2)} = -\left(\tfrac{3495}{64} + \tfrac{1441}{8}n + 225n^2 + \tfrac{3055}{16}n^3 + \tfrac{1965}{32}n^4 + \tfrac{393}{16}n^5\right); \tag{1.8}$$

$$\begin{aligned}\nu = 4, \quad E_n^{(2)} = &-\left(\tfrac{67\,515}{32} + \tfrac{121\,253}{16}n + \tfrac{707\,805}{64}n^2 + \tfrac{685\,685}{64}n^3\right.\\ &\left. + \tfrac{167\,335}{32}n^4 + \tfrac{161\,763}{64}n^5 + \tfrac{27\,895}{64}n^6 + \tfrac{3985}{32}n^7\right);\end{aligned} \tag{1.9}$$

and so on. We note that in all the cases studied, $E_n^{(2)}$ is negative. Also, such problems obey $E_{n+1}^{(2)} < E_n^{(2)}$. Killingbeck [14] extended the procedure of Swenson and Danforth to the radial problem (spherically symmetric and hence non-degenerate levels of the central potential) and found to his surprise that the perturbation λr on the hydrogen atom S-state Hamiltonian, $-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r} - \frac{1}{r}$, once again leads to negative values of $E_n^{(2)}$. We have additionally checked that the above conclusion follows for any $\lambda r^M (M > 1)$ perturbation as well. Here are a few results,

$$\begin{aligned}
M = 1, \quad E_n^{(2)} &= -\left(\tfrac{5}{8}n^4 + \tfrac{7}{8}n^6\right);\\
M = 2, \quad E_n^{(2)} &= -\left(\tfrac{7}{4}n^6 + \tfrac{345}{16}n^8 + \tfrac{143}{16}n^{10}\right);\\
M = 3, \quad E_n^{(2)} &= -\left(\tfrac{621}{32}n^8 + \tfrac{32\,395}{128}n^{10} + \tfrac{10\,829}{32}n^{12} + \tfrac{7365}{128}n^{14}\right);\\
M = 4, \quad E_n^{(2)} &= -\left(\tfrac{1089}{4}n^{10} + \tfrac{297\,505}{64}n^{12} + \tfrac{2167\,431}{256}n^{14} + \tfrac{467\,925}{128}n^{16} + \tfrac{80\,123}{256}n^{16}\right).
\end{aligned} \tag{1.10}$$

Such examples also show that $E_{n+1}^{(2)} < E_n^{(2)}$. This leads us to ask when the second-order energy shift for a non-degenerate state of the Schrödinger equation is always negative. Is there anything special with these two types of problems only?

A few points are worth-noting in the present context. First, the sum for $E_n^{(2)}$ shown in equation (1.5) has both positive and negative terms. For a given energy level n, the contribution of all levels l which have lower eigenvalues is positive while the contribution from the higher states is negative. Therefore, if we conjecture that the second-order energy shift for a non-degenerate state is always negative, it is most likely to fail for the highly excited states, for which the number of positive terms in the sum of equation (1.5) is extremely high. Hence, we would focus attention on large n behavior of $E_n^{(2)}$.

Next we also note that[3]

$$\sum_{j=0}^{n} E_j^{(2)} < 0 \tag{1.11}$$

for any n. In the case of finite-dimensional problems (dimensionality $= N + 1$), n in the above formula can run up to any value $n < N$; but, for $n = N$, we would instead have

$$\sum_{j=0}^{N} E_j^{(2)} = 0. \tag{1.12}$$

This equality makes problems in finite dimensions different from those in infinite ones. If, therefore, we stick to infinite-dimensional problems, we obtain

$$E_0^{(2)} + \sum_{j=1}^{n} E_j^{(2)} < 0 \tag{1.13}$$

for any n. Suppose now that, for a given problem, $E_j^{(2)} \sim Aj^B$ for a quantum number j with A being a constant in the leading order. We can then approximately write, at least for large m,

$$\sum_{j=0}^{m-1} E_j^{(2)} + A\int_m^n j^B\,\mathrm{d}j < 0 \qquad (n > m) \tag{1.14}$$

[3] See [6] for comments on equation (1.11).

and allow the limit $n \to \infty$. For finite $E_0^{(2)}$, one is forced to conclude that $A < 0$ is the only reasonable choice when $B \geqslant -1$. This means $E_j^{(2)} < 0$ for any j in such situations. The cases for which $B < -1$ are then the only potential candidates for showing $E_j^{(2)} > 0$ for $j > 0$. It is tempting to enquire whether a situation of this kind exists.

Thirdly, for a Hamiltonian

$$H = \frac{p^2}{2m} + K|x|^{\mu}, \tag{1.15}$$

if the confining length is L, then the kinetic energy can be estimated as $\frac{n^2\hbar^2}{2mL^2}$ for the nth excited state and the potential energy can be estimated as KL^{μ}. Optimization leads to the critical confining length L_0 given by

$$L_0 \propto n^{\frac{2}{2+\mu}}. \tag{1.16}$$

The n-dependence of the energy is clearly

$$E_n \propto n^{\frac{2\mu}{2+\mu}}. \tag{1.17}$$

For $\mu > 0$, equation (1.17) reveals that $E_n \propto n$ for $\mu = 2$, the standard oscillator case and $E_n \propto n^2$ as $\mu \to \infty$ which corresponds to the infinite square well. On the other hand, if $\mu < 0$ and $K < 0$, then the limit of stability is $\mu = -1$ which corresponds to $E_n \propto n^{-2}$. We thus observe that n-dependence of a bound state for a Hamiltonian of the form of equation (1.15) can range from n^2 to n^{-2}. Therefore, when we perturb a Hamiltonian of the form of equation (1.15), the higher energy levels will cause the least effect if $E_n \propto n^2$. Thus, a perturbation on the infinite square well is most likely to cause a breakdown of the presumption $E_n^{(2)} < 0$. This indeed does happen [15].

Summarizing, should one conjecture that 'the second-order energy shift for a non-degenerate state is always negative', it fails if the unperturbed Hamiltonian is of the infinite square well variety, and is most likely to fail if we consider a highly excited state of the unperturbed Hamiltonian. Since the highly excited states are well described by the Wilson–Sommerfeld quantization condition, we will use that to prove the following: the sufficient condition for the second-order energy shift to be always negative is that both the unperturbed potential and perturbing potential be monotonically increasing and the total potential be symmetric. We establish this result in section 2 and apply it to a few special cases in section 3.

2. A semiclassical proof based on the Wilson–Sommerfeld quantization technique

We note that we need to concentrate on the large quantum numbers where the proposed conjecture, $E_n^{(2)} < 0$, is the weakest. To do it formally, little option is left except adopting some semiclassical scheme. For large quantum numbers, the Wilson–Sommerfeld quantization condition [16] is asymptotically exact. So, it may be employed to gain insight into the problem. To proceed, we consider the Hamiltonian

$$H = \frac{p^2}{2m} + V_0(x) + \lambda V(x). \tag{2.1}$$

Clearly, at the turning point $x = a$, the total energy is the potential energy and given as $E = V_0(a) + \lambda V(a)$. Hence the Wilson–Sommerfeld quantization condition leads to (for symmetric V_0 and V)

$$4\int_0^a \sqrt{E_n - V_0(x) - \lambda V(x)}\,\mathrm{d}x = nh. \tag{2.2}$$

The turning point a will depend on the energy E_n and for every n, we have

$$E_n = V_0(a) + \lambda V(a), \tag{2.3}$$

where both E_n and a have expansions as powers of λ, which can be written as

$$\begin{aligned} E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots, \\ a &= a^{(0)} + \lambda a^{(1)} + \lambda^2 a^{(2)} + \cdots. \end{aligned} \tag{2.4}$$

Using these expansions in equation (2.3), we immediately find by equating the powers of λ

$$a^{(1)} = \frac{E_n^{(1)} - V(a^{(0)})}{V_0'(a^{(0)})}. \tag{2.5}$$

Introducing the expansions of equation (2.4) in equation (2.2), we next have

$$\begin{aligned} \frac{nh}{4} &= \int_0^{a^{(0)}+\lambda a^{(1)}+\lambda^2 a^{(2)}+\cdots} \sqrt{E_n^{(0)} - V_0(x) + \lambda\left[E_n^{(1)} - V(x)\right] + \lambda^2 E_n^{(2)} + \cdots}\,\mathrm{d}x \\ &= \int_0^{a^{(0)}} \sqrt{E_n^{(0)} - V_0(x) + \lambda\left[E_n^{(1)} - V(x)\right] + \lambda^2 E_n^{(2)} + \cdots}\,\mathrm{d}x \\ &\quad + \int_{a^{(0)}}^{a^{(0)}+\lambda a^{(1)}+\lambda^2 a^{(2)}+\cdots} \sqrt{E_n^{(0)} - V_0(x) + \lambda\left[E_n^{(1)} - V(x)\right] + \lambda^2 E_n^{(2)} + \cdots}\,\mathrm{d}x \\ &= \int_0^{a^{(0)}} \sqrt{E_n^{(0)} - V_0(x)}\,\mathrm{d}x + \frac{\lambda}{2}\int_0^{a^{(0)}} \frac{E_n^{(1)} - V(x)}{\sqrt{E_n^{(0)} - V_0(x)}}\,\mathrm{d}x \\ &\quad - \frac{\lambda^2}{8}\int_0^{a^{(0)}} \frac{\mathrm{d}x\left[E_n^{(1)} - V(x)\right]^2}{\left[E_n^{(0)} - V_0(x)\right]^{\frac{3}{2}}}\,\mathrm{d}x + \frac{\lambda^2}{2}E_n^{(2)}\int_0^{a^{(0)}} \frac{\mathrm{d}x}{\sqrt{E_n^{(0)} - V_0(x)}} + \cdots \\ &\quad + \int_{a^{(0)}}^{a^{(0)}+\lambda a^{(1)}+\lambda^2 a^{(2)}+\cdots} \sqrt{E_n^{(0)} - V_0(x) + \lambda\left[E_n^{(1)} - V(x)\right] + \lambda^2 E_n^{(2)} + \cdots}\,\mathrm{d}x. \end{aligned} \tag{2.6}$$

To evaluate the last term on the right-hand side of equation (2.6), we use the result

$$\int_{a^{(0)}}^{a^{(0)}+\Delta} f(x)\,\mathrm{d}x = \Delta f(a^{(0)}) + \frac{\Delta^2}{2} f'(a^{(0)}) + \cdots. \tag{2.7}$$

We can now write equation (2.6) as (up to $O(\lambda^2)$)

$$\begin{aligned} \frac{nh}{4} &= \int_0^{a^{(0)}} \sqrt{E_n^{(0)} - V_0(x)}\,\mathrm{d}x + \frac{\lambda}{2}\int_0^{a^{(0)}} \frac{E_n^{(1)} - V(x)}{\sqrt{E_n^{(0)} - V_0(x)}}\,\mathrm{d}x - \frac{\lambda^2}{8}\int_0^{a^{(0)}} \frac{\mathrm{d}x\left[E_n^{(1)} - V(x)\right]^2}{\left[E_n^{(0)} - V_0(x)\right]^{\frac{3}{2}}}\,\mathrm{d}x \\ &\quad + \frac{\lambda^2}{2}E_n^{(2)}\int_0^{a^{(0)}} \frac{\mathrm{d}x}{\sqrt{E_n^{(0)} - V_0(x)}} + \cdots + [\lambda a^{(1)} + \lambda^2 a^{(2)} + \cdots] \\ &\quad \times \lim_{\epsilon\to 0}\sqrt{E_n^{(0)} - V_0(a^{(0)} - \epsilon) + \lambda\left[E_n^{(1)} - V(a^{(0)} - \epsilon)\right]} \\ &\quad + \frac{1}{2}\lambda^2[a^{(1)}]^2 \lim_{\epsilon\to 0}\frac{-V_0{}'(a^{(0)} - \epsilon)}{2\sqrt{E_n^{(0)} - V_0(a^{(0)} - \epsilon)}} \\ &= \int_0^{a^{(0)}} \sqrt{E_n^{(0)} - V_0(x)}\,\mathrm{d}x + \frac{\lambda}{2}\int_0^{a^{(0)}} \frac{E_n^{(1)} - V(x)}{\sqrt{E_n^{(0)} - V_0(x)}}\,\mathrm{d}x - \frac{\lambda^2}{8}\int_0^{a^{(0)}} \frac{\mathrm{d}x\left[E_n^{(1)} - V(x)\right]^2}{\left[E_n^{(0)} - V_0(x)\right]^{\frac{3}{2}}}\,\mathrm{d}x \end{aligned}$$

$$+\frac{\lambda^2}{2}E_n^{(2)}\int_0^{a^{(0)}}\frac{\mathrm{d}x}{\sqrt{E_n^{(0)}-V_0(x)}}+\cdots+\frac{\lambda^2}{2}a^{(1)}\lim_{\epsilon\to 0}\frac{E_n^{(1)}-V(a^{(0)}-\epsilon)}{\sqrt{E_n^{(0)}-V_0(a^{(0)}-\epsilon)}}$$

$$-\frac{\lambda^2}{4}[a^{(1)}]^2\lim_{\epsilon\to 0}\frac{V_0{}'(a^{(0)}-\epsilon)}{\sqrt{E_n^{(0)}-V_0(a^{(0)}-\epsilon)}}. \tag{2.8}$$

Equating the identical powers of λ from the two sides of equation (2.8) and using $a^{(1)}$ from equation (2.5), we get

$$\int_0^{a^{(0)}}\sqrt{E_n^{(0)}-V_0(x)}\,\mathrm{d}x=\frac{nh}{4}, \tag{2.9}$$

$$E_n^{(1)}=\frac{\int_0^{a^{(0)}}\frac{V(x)\,\mathrm{d}x}{\sqrt{E_n^{(0)}-V_0(x)}}}{\int_0^{a^{(0)}}\frac{\mathrm{d}x}{\sqrt{E_n^{(0)}-V_0(x)}}}, \tag{2.10}$$

and

$$E_n^{(2)}\int_0^{a^{(0)}}\frac{\mathrm{d}x}{\sqrt{E_n^{(0)}-V_0(x)}}=\frac{1}{4}\int_0^{a^{(0)}}\frac{\mathrm{d}x\big[E_n^{(1)}-V(x)\big]^2}{\big[E_n^{(0)}-V_0(x)\big]^{\frac{3}{2}}}$$

$$-\frac{1}{2}\lim_{\epsilon\to 0}\frac{\big[E_n^{(1)}-V(a^{(0)})\big]^2}{V_0'(a^{(0)})\sqrt{E_n^{(0)}-V_0(a^{(0)}-\epsilon)}}. \tag{2.11}$$

We note that the term on the right-hand side of equation (2.11) diverges as $\epsilon\to 0$, but we will show below that this divergence cancels with the divergence coming from the integral in the first term and the resulting $E_n^{(2)}$ is finite.

We first treat the divergence in the first integral on the right-hand side. This integral can be written as

$$\frac{1}{4}\int_0^{a^{(0)}}\frac{\mathrm{d}x\big[E_n^{(1)}-V(x)\big]^2}{\big[E_n^{(0)}-V_0(x)\big]^{\frac{3}{2}}}=\frac{1}{4}\int_0^{a^{(0)}}\frac{\mathrm{d}x\big[E_n^{(1)}-V(x)\big]^2-\big[E_n^{(1)}-V(a^{(0)})\big]^2}{\big[E_n^{(0)}-V_0(x)\big]^{\frac{3}{2}}}$$

$$+\frac{1}{4}\int_0^{a^{(0)}}\frac{\mathrm{d}x\big[E_n^{(1)}-V(a^{(0)})\big]^2}{\big[E_n^{(0)}-V_0(x)\big]^{\frac{3}{2}}}$$

$$=\frac{1}{4}\int_0^{a^{(0)}}\frac{\mathrm{d}x\big[E_n^{(1)}-V(x)\big]^2-\big[E_n^{(1)}-V(a^{(0)})\big]^2}{\big[E_n^{(0)}-V_0(x)\big]^{\frac{3}{2}}}$$

$$+\frac{1}{4}\big[E_n^{(1)}-V(a^{(0)})\big]^2\int_0^{a^{(0)}}\frac{\mathrm{d}x}{[V_0(a^{(0)})-V_0(x)]^{\frac{3}{2}}}. \tag{2.12}$$

Substituting $y=a^{(0)}-x$, we can write

$$\int_0^{a^{(0)}}\frac{\mathrm{d}x}{[V_0(a^{(0)})-V_0(x)]^{\frac{3}{2}}}=\int_0^{a^{(0)}}\frac{\mathrm{d}y}{[V_0(a^{(0)})-V_0(a^{(0)}-y)]^{\frac{3}{2}}}$$

$$=\left[\int_0^{a^{(0)}}\frac{\mathrm{d}y}{[V_0(a^{(0)})-V_0(a^{(0)}-y)]^{\frac{3}{2}}}-\int_0^{a^{(0)}}\frac{\mathrm{d}y}{y^{\frac{3}{2}}\left(\frac{\delta V_0}{\delta a}\right)^{\frac{3}{2}}}+\int_0^{a^{(0)}}\frac{\mathrm{d}y}{y^{\frac{3}{2}}\left(\frac{\delta V_0}{\delta a}\right)^{\frac{3}{2}}}\right]$$

$$= \left[\int_0^{a^{(0)}} \frac{\mathrm{d}y}{[V_0(a^{(0)}) - V_0(a^{(0)} - y)]^{\frac{3}{2}}} - \int_0^{a^{(0)}} \frac{\mathrm{d}y}{y^{\frac{3}{2}} \left(\frac{\delta V_0}{\delta a}\right)^{\frac{3}{2}}} + \lim_{\epsilon \to 0} \int_\epsilon^{a^{(0)}} \frac{\mathrm{d}y}{y^{\frac{3}{2}} \left(\frac{\delta V_0}{\delta a}\right)^{\frac{3}{2}}} \right]$$

$$= \left[\int_0^{a^{(0)}} \frac{y^{\frac{3}{2}} \left(\frac{\delta V_0}{\delta a}\right)^{\frac{3}{2}} - [V_0(a^{(0)}) - V_0(a^{(0)} - y)]^{\frac{3}{2}}}{y^{\frac{3}{2}} \left(\frac{\delta V_0}{\delta a}\right)^{\frac{3}{2}} [V^0(a^{(0)}) - V_0(a^{(0)} - y)]^{\frac{3}{2}}} \mathrm{d}y \right.$$

$$\left. + \lim_{\epsilon \to 0} \frac{1}{2\left(\frac{\delta V_0}{\delta a}\right)^{\frac{3}{2}}} \left(\frac{1}{\epsilon^{\frac{1}{2}}} - \frac{1}{a^{(0)\frac{1}{2}}} \right) \right]. \tag{2.13}$$

Now the second term on the right-hand side of equation (2.11) can be written as

$$\lim_{\epsilon \to 0} \frac{1}{2} \frac{\left[E_n^{(1)} - V(a^{(0)})\right]^2}{V_0'(a^{(0)}) \sqrt{E_n^{(0)} - V_0(a^{(0)} - \epsilon)}} = \lim_{\epsilon \to 0} \frac{1}{2} \frac{\left[E_n^{(1)} - V(a^{(0)})\right]^2}{V_0'(a^{(0)}) \sqrt{V_0(a^{(0)}) - V_0(a^{(0)} - \epsilon)}}$$

$$= \lim_{\epsilon \to 0} \frac{1}{2} \frac{\left[E_n^{(1)} - V(a^{(0)})\right]^2}{V_0'(a^{(0)})^{\frac{3}{2}} \sqrt{\epsilon}}. \tag{2.14}$$

Putting these expressions in equation (2.11) we get the final expression as

$$E_n^{(2)} \int_0^a \frac{\mathrm{d}x}{\sqrt{E^{(0)} - V_0(x)}} = \frac{1}{4} \left[E_n^{(1)} - V(a^{(0)})\right]^2$$

$$\times \left[-\frac{1}{2} \frac{1}{\left(\frac{\delta V_0}{\delta a}\right)^{\frac{3}{2}}} \frac{1}{a^{(0)\frac{1}{2}}} + \int_0^{a^{(0)}} \frac{x^{\frac{3}{2}} \left(\frac{\delta V_0}{\delta a}\right)^{\frac{3}{2}} - [V_0(a^{(0)}) - V_0(a^{(0)} - x)]^{\frac{3}{2}}}{x^{\frac{3}{2}} \left(\frac{\delta V_0}{\delta a}\right)^{\frac{3}{2}} [V_0(a^{(0)}) - V_0(a^{(0)} - x)]^{\frac{3}{2}}} \mathrm{d}x \right]$$

$$+ \frac{1}{4} \int_0^{a^{(0)}} \frac{\mathrm{d}x [V(x)^2 - V(a^{(0)})^2 - 2E_n^{(1)}(V(x) - V(a^{(0)}))]}{\left[E_n^{(0)} - V_0(x)\right]^{\frac{3}{2}}}. \tag{2.15}$$

We now need to examine the various terms on the right-hand side of equation (2.15). The first term

$$-\frac{1}{8} \frac{\left[E_n^{(1)} - V(a^{(0)})\right]^2}{\left(\frac{\delta V_0}{\delta a}\right)^{\frac{3}{2}} (a^{(0)})^{\frac{1}{2}}}$$

is clearly negative. The sign of the second term depends on the sign of

$$x^{\frac{3}{2}} \left(\frac{\delta V_0}{\delta a}\right)^{\frac{3}{2}} - [V_0(a^{(0)}) - V_0(a^{(0)} - x)]^{\frac{3}{2}}.$$

If $V_0(x)$ is a monotonic function of x then the difference $V_0(a^{(0)}) - V_0(a^{(0)} - x)$ is always greater than the 'straight-line' approximation of $\frac{\delta V_0}{\delta a} x$ and thus the quantity under consideration is negative. If we now turn to the third term, we note that it can be written as

$$\frac{1}{4} \int_0^{a^{(0)}} \frac{\mathrm{d}x [V(x) - V(a^{(0)})]\left[V(x) + V(a^{(0)}) - 2E_n^{(1)}\right]}{\left[E_n^{(0)} - V_0(x)\right]^{\frac{3}{2}}}.$$

Looking at this integral, we note that most of the contribution comes from the vicinity of $x = a^{(0)}$ where the integral is singular. Consequently, we approximate the weighting function of $V(x) + V(a^{(0)}) - 2E_n^{(1)}$ by its $x \to a^{(0)}$ limit which works out to be

$$-\frac{1}{6} \frac{V'(a^{(0)})}{V_0'(a^{(0)})} \frac{1}{\left[E_n^{(0)} - V_0(x)\right]^{\frac{1}{2}}}.$$

Therefore, the integral can be written as

$$-\frac{1}{6}\frac{V'(a^{(0)})}{V_0'(a^{(0)})}\int_0^{a^{(0)}}\frac{V(x)+V(a^{(0)})-2E_n^{(1)}}{\left[E_n^{(0)}-V_0(x)\right]^{\frac{1}{2}}}\,\mathrm{d}x=\frac{1}{6}\frac{V'(a^{(0)})}{V_0'(a^{(0)})}\int_0^{a^{(0)}}\frac{V(a^{(0)})-E_n^{(1)}}{\left[E_n^{(0)}-V_0(x)\right]^{\frac{1}{2}}}\,\mathrm{d}x, \tag{2.16}$$

where we have used the form of $E_n^{(1)}$ (see equation (2.10)) to obtain the above expression. Since $E_n^{(1)}$ is the average value of $V(x)$ over a distribution normalized to unity, $V(a^{(0)}) > E_n^{(1)}$ and hence the expression on the right-hand side of equation (2.16) is always negative provided $V'(a^{(0)})$ and $V_0'(a^{(0)}) > 0$. We thus finally find that all the terms on the right-hand side of equation (2.15) are negative if $V(x)$ and $V_0(x)$ are monotonically increasing functions of x. This is the central result of the paper.

3. Some applications and discussion

To illustrate the consistency of our result we examine the Hamiltonian

$$H=\frac{p^2}{2m}+kx^{2\mu}+\lambda x^{2\nu} \tag{3.1}$$

for arbitrary μ and ν. For arbitrary μ and ν the second-order energy expression is virtually useless to estimate the correction to the ground-state energy. Consequently, we treat the Hamiltonian of equation (3.1) through the Wilson–Sommerfeld condition. In this case, we have

$$\oint\sqrt{2m(E-kx^{2\mu}-\lambda x^{2\nu})}\,\mathrm{d}x=nh. \tag{3.2}$$

Obviously, the kinetic energy is zero when the displacement from the equilibrium position reaches its maximum value, i.e. $x = a$ where a is the amplitude. Hence the total energy of the system becomes

$$E=ka^{2\mu}+\lambda a^{2\nu}. \tag{3.3}$$

Inserting equation (3.3) in equation (3.2) and expanding to $O(\lambda^2)$ leads to

$$a^{\mu+1}I_1+\frac{\lambda}{2k}a^{1+2\nu-\mu}I_2-\frac{\lambda^2}{8k^2}a^{4\nu-3\mu-1}I_3=\frac{nh}{4\sqrt{k}}, \tag{3.4}$$

where

$$I_1=\frac{1}{2\mu}\frac{\Gamma\left(\frac{1}{2\mu}\right)\Gamma\left(\frac{3}{2}\right)}{\Gamma\left(\frac{1}{2\mu}+\frac{3}{2}\right)}, \tag{3.5}$$

$$I_2=\frac{1}{2\mu}\left[\frac{\Gamma\left(\frac{1}{2\mu}\right)}{\Gamma\left(\frac{1}{2\mu}+\frac{1}{2}\right)}-\frac{\Gamma\left(\frac{1+2\nu}{2\mu}\right)}{\Gamma\left(\frac{1+2\nu}{2\mu}+\frac{1}{2}\right)}\right]\Gamma\left(\frac{1}{2}\right), \tag{3.6}$$

$$I_3=\frac{1}{2\mu}\left[\frac{2\left(\frac{1+2\nu}{2\mu}-\frac{1}{2}\right)\Gamma\left(\frac{1+2\nu}{2\mu}\right)}{\Gamma\left(\frac{1+2\nu}{2\mu}+\frac{1}{2}\right)}-\frac{\left(\frac{1+4\nu}{2\mu}-\frac{1}{2}\right)\Gamma\left(\frac{1+4\nu}{2\mu}\right)}{\Gamma\left(\frac{1+4\nu}{2\mu}+\frac{1}{2}\right)}-\frac{\left(\frac{1-\mu}{2\mu}\right)\Gamma\left(\frac{1}{2\mu}\right)}{\Gamma\left(\frac{1}{2\mu}+\frac{1}{2}\right)}\right]\Gamma\left(\frac{1}{2}\right). \tag{3.7}$$

Using expansions given in equation (2.4) in equation (3.3), a straightforward algebra leads to

$$E_n^{(2)}=\frac{\mu}{2k}{a_0}^{4\nu-2\mu}\left[\frac{1}{\mu+1}\frac{I_3}{I_1}+\frac{\left(2\nu-\frac{\mu}{2}+\frac{1}{2}\right)}{(\mu+1)^2}\frac{{I_2}^2}{{I_1}^2}-\frac{2\nu}{\mu(\mu+1)}\frac{I_2}{I_1}\right], \tag{3.8}$$

where

$$a_0 = \frac{\mu n h}{2\sqrt{k}} \frac{\Gamma\left(\frac{1}{2\mu} + \frac{3}{2}\right)}{\Gamma\left(\frac{1}{2\mu}\right)\Gamma\left(\frac{3}{2}\right)}.$$

As a special case, when $\mu = \nu$, we get the simple expression of second-order energy shift as

$$E_n^{(2)} = -\mu \frac{{a_0}^{2\mu}}{2k} \frac{1}{(1+\mu)^2} \tag{3.9}$$

which is negative definite. If we put $\mu = 1$ and $k = \frac{1}{2}m\omega^2$, the Hamiltonian of equation (3.1) reduces to Hamiltonian of equation (1.6) with the second-order energy shift

$$E_n^{(2)} = \left(\sqrt{\frac{nh}{\pi}}\frac{1}{(km)^{\frac{1}{4}}}\right)^{4\nu-2} \left[\frac{4\nu}{2\pi k}\left\{\frac{\Gamma\left(\nu+\frac{1}{2}\right)}{\Gamma(\nu+1)} - \sqrt{\pi}\right\} + \frac{1}{\sqrt{\pi}k}\left\{\frac{2\Gamma\left(\nu+\frac{1}{2}\right)}{\Gamma(\nu)} - \frac{\Gamma\left(2\nu+\frac{1}{2}\right)}{\Gamma(2\nu)}\right\} + \frac{2\nu}{\sqrt{\pi k}}\frac{\Gamma\left(\nu+\frac{1}{2}\right)}{\Gamma(\nu+1)} - \sqrt{\pi}\right]. \tag{3.10}$$

Now we may put $\nu = 1, 2, \ldots$ in the above expression of $E_n^{(2)}$ to get the following results,

$${E_n}^{(2)} = -\frac{n\hbar}{2m^2\omega^3}, \qquad \nu = 1 \tag{3.11}$$

$${E_n}^{(2)} = -\frac{17n^3\hbar^3}{4m^4\omega^5}, \qquad \nu = 2 \tag{3.12}$$

$${E_n}^{(2)} = -\frac{393n^5\hbar^5}{16m^6\omega^7}, \qquad \nu = 3 \tag{3.13}$$

$${E_n}^{(2)} = -\frac{3985n^7\hbar^7}{32m^8\omega^9}, \qquad \nu = 4 \tag{3.14}$$

and so on. These results agree with the term carrying the largest power of n in equations (1.7)–(1.9), as expected. The asymptotic limit, when ν is very large, yields

$${E_n}^{(2)} = -\frac{\left(\sqrt{\frac{nh}{\pi}}\frac{1}{(km)^{\frac{1}{4}}}\right)^{4\mu}}{\pi k} 2\nu(\sqrt{\nu}). \tag{3.15}$$

This expression explicitly shows that the second-order energy shift is negative for large ν for any n.

More interesting is to study the case with $\nu = 1$, but μ arbitrary. The Hamiltonian becomes

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^{2\mu} + \lambda x^2.$$

The important point to note here is that the solution of the unperturbed problem $H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$, which is essential for the standard perturbation theory, is not known in closed form. But, using the Wilson–Sommerfeld technique, we should be able to get the correct answer for the energy levels when the quantum number is large. To proceed with, we employ the expression for $E_n^{(2)}$, as given in equation (3.8), and now set $\nu = 1$ to obtain

$$E_n^{(2)} = \frac{\mu}{2k}{a_0}^{4-2\mu}\left[\frac{1}{\mu+1}\frac{I_3}{I_1} + \frac{\left(2-\frac{\mu}{2}+\frac{1}{2}\right)}{(\mu+1)^2}\frac{{I_2}^2}{{I_1}^2} - \frac{2}{\mu(\mu+1)}\frac{I_2}{I_1}\right]. \tag{3.16}$$

We then find

$$a^{(0)} = \left(\frac{2n\hbar}{m\omega}\right)^{\frac{1}{\mu+1}}. \tag{3.17}$$

Putting the value of $\mu = 2$, we get

$$E_n^{(2)} = -\frac{n\hbar}{2m^2\omega^3} \tag{3.18}$$

which is negative, and is the same as equation (3.11). This can be seen to be correct as, with this value of μ, the problem reduces to a simple harmonic oscillator with a modified angular velocity ω':

$$\omega' = \sqrt{\omega^2 + \frac{2\lambda}{m}}. \tag{3.19}$$

It is the asymptotic limit, when μ is very large, which is of particular interest. In this case, we find from equation (3.16)

$$E_n^{(2)} = -\frac{34}{45\left(\frac{2n\hbar}{m\omega}\right)^{\frac{2\mu}{\mu+1}}}. \tag{3.20}$$

The second-order energy shift is once again negative in accordance with the theorem of section 3. However, it is interesting to note that here $E_n^{(2)} \sim n^{-\frac{2\mu}{1+\mu}}$, so that $E_n^{(2)}$ falls off faster than $\frac{1}{n}$ for large n. In section 1, we had noted that this is a potential problem case (see the discussion below equation (2.4)). The fact that we still get a negative shift is a consequence of the weaker condition of the actual theorem.

We next take a situation where $V(x)$ is not monotonically increasing and consider the Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2 + \lambda(x^6 - \alpha^2 x^4). \tag{3.21}$$

Here the unperturbed Hamiltonian is $H_0 = \frac{p^2}{2m} + \frac{1}{2}kx^2$, and the perturbation is $H' = \lambda(x^6 - \alpha^2 x^4)$. Using the Wilson–Sommerfeld technique we should be able to get the correct answer for the energy levels when the quantum number is large. The kinetic energy is zero when the displacement from the equilibrium position reaches its maximum value, i.e. $x = a$, where a is the amplitude, and hence the total energy of the system is

$$E = \tfrac{1}{2}ka^2 + \lambda(a^6 - \alpha^2 a^4). \tag{3.22}$$

Now using the Wilson–Sommerfeld quantization rule followed by expansion (3.4) and subsequently equating order by order, we get

$$E_n^{(0)} = n\hbar\omega, \tag{3.23}$$

$$E_n^{(1)} = \frac{5}{16}\left(\frac{nh}{\pi m\omega}\right)^3 - \frac{3}{8}\alpha^2\left(\frac{nh}{\pi m\omega}\right)^2, \tag{3.24}$$

$$E_n^{(2)} = \frac{1}{512}\frac{1}{m\omega^2}\left(\frac{nh}{\pi m\omega}\right)^3\left[-393\left(\frac{nh}{\pi m\omega}\right)^2 + 660\alpha^2\left(\frac{nh}{\pi m\omega}\right) - 272\alpha^4\right]. \tag{3.25}$$

It is easy to see from equation (3.25) that *a range of* α exists over which the second-order energy shift becomes positive, thereby exhibiting the negative content of the theorem.

We end this discussion by pointing out an interesting effect of the symmetry of the potential. We turn to the scenario where a negative second-order shift can be most easily jeopardised as explained before—a situation of large quantum numbers and unperturbed energy proportional to n^2. This is the particle in a box problem located, suppose, between

$x = 0$ and $x = L$. The perturbing potential is chosen as an attractive delta function placed at $x = pL$ with $0 < p < 1$. The Schödinger equation then reads

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x) - \lambda\delta(x - pL)\psi(x) = E\psi(x). \tag{3.26}$$

Matching across the δ-function, we find for the second-order shift

$$E_n^{(2)} = -\frac{2m}{\hbar^2}\left[\frac{\sin^2(n\pi p)}{n^2\pi^2} + \frac{1-2p}{n\pi}\sin(2n\pi p)\sin^2(n\pi p)\right]. \tag{3.27}$$

The shift is negative definite for any n at $p = \frac{1}{2}$, but *not* so at other values of p. If $p = \frac{1}{4}$, we have found, for example, that $E_n^{(2)}$ is positive for $n = 7$. What is the difference between $p = \frac{1}{2}$ and other values of p? For $p = \frac{1}{2}$, we note that the perturbation maintains the symmetry that the original Hamiltonian had about $x = \frac{L}{2}$. We now ask whether the second-order shift is guaranteed to be negative if the perturbation respects the symmetry of the Hamiltonian (for a one-dimensional problem, this is just the reflection symmetry). With this in mind, we consider the same problem but now with two attractive delta function potentials, one at $x = pL$ and another at $x = qL$ with $0 < p < 1$ and $0 < q < 1$. Then, the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x) - \lambda\left[\delta(x - pL) + \delta(x - qL)\right]\psi(x) = E\psi(x). \tag{3.28}$$

After some simple algebra, we get the second-order energy shift as

$$E_n^{(2)} = \frac{8m}{\hbar^2\pi^2}\left[\sin^2\{n\pi p\}\sum_{l\neq n}\frac{\sin^2\{l\pi p\}}{n^2 - l^2} + \sin^2\{n\pi q\}\sum_{l\neq n}\frac{\sin^2\{l\pi q\}}{n^2 - l^2}\right.$$
$$\left. + 2\sin(n\pi p)\sin(n\pi q)\sum_{l\neq n}\frac{\sin(l\pi p)\sin(l\pi q)}{n^2 - l^2}\right]. \tag{3.29}$$

In this case, the second-order energy shift for an arbitrary state is negative not for all symmetric dispositions of p and q, but only for some *special* case when $p = \frac{1}{4}$ and $q = \frac{3}{4}$. It may be pedagogically worthwhile analyzing why this is so.

4. Conclusion

In perturbation theory, the first nontrivial correction to energy involving, in general, all the energy eigenstates appears at the second-order. This second-order correction also corresponds to the leading response property of the system in the given state. Therefore, the importance of $E_n^{(2)}$ among all $E_n^{(m)}$ is rather obvious. However, while the inequality $E_0^{(2)} < 0$ holds for any perturbation on any system, it is generally impossible to predict the sign of $E_n^{(2)} (n \neq 0)$ even for simple model systems with specific perturbations.

We have, on the other hand, found that an infinitude of perturbations acting either on the harmonic oscillator Hamiltonian or the H-atom Hamiltonian lead to the inequality $E_n^{(2)} < 0$ for any n. Such an observation calls for a closure scrutiny in respect of both the unperturbed problem and the nature of the perturbation. Our preliminary investigations have revealed that (i) a breakdown of $E_n^{(2)} < 0$ is more likely for larger n, (ii) if $|E_n^{(2)}|$ increases with n, then one would certainly find that $E_n^{(2)} < 0$ (see, e.g., the discussion around equation (1.13)) and (iii) the nature of the zero order energy spectrum plays a crucial role in this context, and thus the negativity of $E_n^{(2)} < 0$ is more favorable, for example in the case of perturbations on the

H-atom than perturbations on the particle in a box. We next explored whether the problem can be handled quantitatively via a semiclassical scheme. This serves two purposes. First, it simplifies the analysis that would otherwise have not been possible had we gone for a strict quantum-mechanical proof. Secondly, a semiclassical scheme approaches exactness in the large-n limit, and precisely in such situations $E_n^{(2)} < 0$ is more likely to be invalid. Hence , if the inequality sought is obeyed in a semiclassical context, it is likely to be valid in quantum domain too at lower n values.

The present work shows that, if the unperturbed and perturbing potentials are both monotonically increasing, and the total potential is symmetric, then the inequality $E_n^{(2)} < 0$ follows. This is a sufficient condition but encompasses the observations mentioned in section 1. For the H-atom problem, a conversion to the one-dimensional form will lead to similar conclusion as obtained in section 2. We have also checked that the results for the potential $\frac{1}{2}m\omega^2 + \lambda x^{2\mu}$ found from the second-order perturbation theory and from the Wilson–Sommerfeld condition agree in the leading n part. More interestingly, while a perturbation of the form λx^2 on the particle in a box problem produces a positive $E_n^{(2)}$ for large n, the same perturbation acting on a $x^{2\mu}$ potential (unperturbed) shows $E_n^{(2)} < 0$ at any $\mu \gg 1$. Note that the latter problem is not amenable to quantum mechanics properly owing to the lack of exact solution for the unperturbed eigenvalue problem. However, the Wilson–Sommerfeld scheme ensures rightly that the unperturbed spectrum for $\mu \gg 1$ goes almost as n^2, very much like the box problem. It is here that the importance of the monotonically increasing potential is made quite apparent. We hope further work along this line may lead to a lot more interesting and important conclusions that would similarly be relevant to proper quantum mechanics as well.

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