3.7.4 HARMONIC OSCILLATOR PERTURBATIONS

The perturbation algorithm for energy corrections may be applied for any completely solved isolated system, of which, apart of hydrogenic ones, the harmonic oscillator represents an important application for modeling molecular open states. There will be considered two cases of perturbations: one having the symmetric coordinate perturbation, while the second is linear in coordinate with a constant that may represent some external electric intensity.

1. Starting with the harmonic oscillator with the unperturbed Hamiltonian

$$\widehat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{k_{\omega_0}}{2}\hat{x}^2, \quad k_{\omega_0} = m\omega_0^2 \tag{3.555}$$

with the associate spectrum

$$\varepsilon_n = \hbar\omega_0\left(n + \frac{1}{2}\right), n \in \mathrm{N} \tag{3.556}$$

one searches for its correction produced by the existence of the perturbation Hamiltonian:

$$\widehat{H}_1 = \frac{b}{2}\hat{x}^2, \ b \in \mathrm{R} \tag{3.557}$$

The direct way of determining the spectrum corrections relays on composing the total Hamiltonian as

$$\widehat{H} = \widehat{H}_0 + \widehat{H}_1 = \frac{\hat{p}^2}{2m} + \frac{k_{\omega_0} + b}{2}\hat{x}^2 \tag{3.558}$$

and to identify from it the new oscillating frequency (due to inclusion of perturbation) throughout

$$k_{\omega_0} + b = m\omega^2$$
$$\Rightarrow \omega = \sqrt{\frac{k_{\omega_0} + b}{m}} = \underbrace{\sqrt{\frac{k_{\omega_0}}{m}}}_{\omega_0}\sqrt{1 + \frac{b}{k_{\omega_0}}} = \omega_0\sqrt{1 + \frac{b}{k_{\omega_0}}} \tag{3.559}$$

which can be expanded in series up to the desired order, say two, in terms of "*b*" perturbation, using the series expansion according with the McLaurin formula

$$\sqrt{1+\bullet} \cong 1+\frac{\bullet}{2}-\frac{\bullet^2}{8} \tag{3.560}$$

to obtain the perturbed frequency:

$$\omega \cong \omega_0\left(1+\frac{b}{2k_{\omega_0}}-\frac{b^2}{8k_{\omega_0}^2}\right) \tag{3.561}$$

and then by means of direct substitution back on the original spectra the perturbed energy is provided

$$\mathrm{E}_n \cong \varepsilon_n + \frac{b}{2k_{\omega_0}}\varepsilon_n - \frac{b^2}{8k_{\omega_0}^2}\varepsilon_n \tag{3.562}$$

from where the first and second energy corrections are individually identified as:

$$\mathrm{E}_n^{(1)} = \frac{b}{2k_{\omega_0}}\varepsilon_n \tag{3.563}$$

$$\mathrm{E}_n^{(2)} = -\frac{b^2}{8k_{\omega_0}^2}\varepsilon_n \tag{3.564}$$

Yet, there is noted that in fact no use of the perturbation algorithm was made in deriving these corrections; therefore some cross-check is require. This can be done either using the properties of Hermite polynomials in employing the wave-functions of harmonic oscillator, or, more elegantly, through further employing the quantum information contained into the Heisenberg matrix approach. For the future purposes the second way is here unfolded. We have to actually compute the matrices elements $\langle n|\widehat{H}_1|n\rangle$ and $\langle n'|\widehat{H}_1|n\rangle$, $n, n' \in \mathrm{N}$ for computing the first and second order energy corrections, respectively. That means, we have in fact to compute the quantities $\langle n|\hat{x}^2|n\rangle$ and $\langle n'|\hat{x}^2|n\rangle$, leading with idea that the coordinate matrix $[x]$ has to be somehow further exploited from the Heisenberg matrix theory of harmonic oscillator. In this respect one may observe two important things with the coordinate $[Q]$ matrix derived in Section 2.4.6:

- The matrix is symmetrical due to the symmetry of the harmonic potential, thus allows identification

$$q_{n-1,n} = q_{n,n-1} \tag{3.565}$$

with the help of which they can be computed from their combined relationship as:

$$q_{n-1,n} = q_{n,n-1} = \frac{\alpha}{\sqrt{2}}\sqrt{n},\ \ \alpha = \sqrt{\frac{\hbar}{m\omega_0}} \tag{3.566}$$

to provide the rewritten of the harmonic oscillator coordinate matrix as:

$$[x] = \frac{\alpha}{\sqrt{2}}\begin{bmatrix} 0 & 1 & 0 & \cdots \\ 1 & 0 & \sqrt{2} & \cdots \\ 0 & \sqrt{2} & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \tag{3.567}$$

- This matrix may be seen as being composed by two different matrices,

$$[x] = \frac{\alpha}{\sqrt{2}}\left([a^+] + [a]\right) \tag{3.568}$$

one for the upper diagonal and other for the down diagonal rows of $\sqrt{n}$ quantum numbers; accordingly they may be eventually called annihilation $[a]$ and creation $[a^+]$ matrices (with associate operators, of course) for the reason bellow revealed, however displaying like:

$$[a] = \begin{bmatrix} 0 & 1 & 0 & \cdots \\ 0 & 0 & \sqrt{2} & \cdots \\ 0 & 0 & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix},\quad [a^+] = \begin{bmatrix} 0 & 0 & 0 & \cdots \\ 1 & 0 & 0 & \cdots \\ 0 & \sqrt{2} & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \tag{3.569}$$

In terms of operators, the coordinate operator relationship with annihilation and creation operators reads

$$\hat{x} = \frac{\alpha}{\sqrt{2}}\left(\hat{a}^+ + \hat{a}\right) \tag{3.570}$$

while for the matrix elements there is found through inspection of above matrices the operatorial rules:

$$\langle n'|\hat{a}|n\rangle = \sqrt{n}\delta_{n',n-1} = \sqrt{n}\langle n'|n-1\rangle \tag{3.571}$$

$$\langle n'|\hat{a}^{+}|n\rangle = \sqrt{n+1}\delta_{n',n+1} = \sqrt{n+1}\langle n'|n+1\rangle \tag{3.572}$$

assuming the quantum numbers' combinations $(n'=0, n=1)$ and $(n'=1, n=0)$ so that at extreme the annihilation operator to act over the state with $n=1$ (i.e., to have something the "annihilate") while the creation operator applies on the state with $n=0$ (i.e., to have to create something from " nothing"). Moreover, these combinations generates the first matrix element (equal to "1") above and bellow the diagonal in matrices of annihilation and creation operators (when the matrices structures are defined as beginning with 0th line and 0th column, respectively); as such, these matrices are said to be written in the particle's "number" representation, since rooting on the quantum numbers. More details and extensions of these ideas are to be presented with occasion of many-body quantum systems discussion, latter on. For the moment one retains the annihilation and creation operatorial actions:

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle \tag{3.573}$$

$$\hat{a}^{+}|n\rangle = \sqrt{n+1}|n+1\rangle \tag{3.574}$$

abstracted from above matrices' elements.

For the shake of completeness, note that in the same manner the analysis of the Heisenberg momentum matrix provides the particle's representation as:

$$[p] = \frac{i\beta}{\sqrt{2}}\begin{bmatrix} 0 & -1 & 0 & \cdots \\ 1 & 0 & -\sqrt{2} & \cdots \\ 0 & \sqrt{2} & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} = \frac{i\beta}{\sqrt{2}}\left([a^{+}]-[a]\right),\ \beta = \sqrt{\hbar m\omega_0} \tag{3.575}$$

with the correspondent operatorial connection with creation and annihilation operators:

$$\hat{p} = \frac{\alpha}{\sqrt{2}}\left(\hat{a}^{+} - \hat{a}\right) \tag{3.576}$$

Now, having rewritten the coordinate matrix elements with the help of creation and annihilation matrix elements as well will highly help our perturbation calculation since preserving the absolute generality (i.e., not restraining the checking only to the ground state for instance) and involving the so-called "shifted diagonalization" or delta-Kronecker rules that elegantly select the mixed contributing states to the energy.

Let's proceed with the first order correction to successively get:

$$
\begin{aligned}
\mathrm{E}_n^{(1)} &= \langle n|\hat{H}_1|n\rangle = \frac{b}{2}\langle n|\hat{x}^2|n\rangle = \frac{b}{2}\langle n|\left[\frac{\alpha}{\sqrt{2}}\left(\hat{a}^{+} + \hat{a}\right)\right]^2|n\rangle \\
&= \frac{b\alpha^2}{4}\langle n|\left(\hat{a}^{+}\hat{a}^{+} + \hat{a}^{+}\hat{a} + \hat{a}\hat{a}^{+} + \hat{a}\hat{a}\right)|n\rangle \\
&= \frac{b\alpha^2}{4}[\langle n|\hat{a}^{+}\underbrace{\hat{a}^{+}|n\rangle}_{\sqrt{n+1}|n+1\rangle} + \langle n|\hat{a}^{+}\underbrace{\hat{a}|n\rangle}_{\sqrt{n}|n-1\rangle} + \langle n|\hat{a}\underbrace{\hat{a}^{+}|n\rangle}_{\sqrt{n+1}|n+1\rangle} + \langle n|\hat{a}\underbrace{\hat{a}|n\rangle}_{\sqrt{n}|n-1\rangle}] \\
&= \frac{b\alpha^2}{4}[\sqrt{n+1}\langle n|\underbrace{\hat{a}^{+}|n+1\rangle}_{\sqrt{n+2}|n+2\rangle} + \sqrt{n}\langle n|\underbrace{\hat{a}^{+}|n-1\rangle}_{\sqrt{n}|n\rangle} \\
&\quad + \sqrt{n+1}\langle n|\underbrace{\hat{a}|n+1\rangle}_{\sqrt{n+1}|n\rangle} + \sqrt{n}\langle n|\underbrace{\hat{a}|n-1\rangle}_{\sqrt{n-1}|n-2\rangle}] \\
&= \frac{b\alpha^2}{4}[\sqrt{(n+1)(n+2)}\underbrace{\langle n|n+2\rangle}_{0} + n\underbrace{\langle n|n\rangle}_{1} \\
&\quad + (n+1)\underbrace{\langle n|n\rangle}_{1} + \sqrt{n(n-1)}\underbrace{\langle n|n-2\rangle}_{0}] \\
&= \frac{b\alpha^2}{2}\left(n + \frac{1}{2}\right) \\
&= \frac{b\alpha^2}{2\hbar\omega_0}\underbrace{\hbar\omega_0\left(n + \frac{1}{2}\right)}_{\varepsilon_n} = \frac{b}{2\hbar\omega_0}\frac{\hbar}{m\omega_0}\varepsilon_n = \frac{b}{2k_{\omega_0}}\varepsilon_n
\end{aligned}
\tag{3.577}
$$

thus regaining exactly the same expression as from direct series expansion, nevertheless proofing both the perturbation as well as annihilation-creation operatorial formalisms.

Going to checkout the second order correction we have to evaluate:

$$\mathrm{E}_n^{(2)} = \sum_{n' \neq n} \frac{\left|\left\langle n' \middle| \widehat{H}_1 \middle| n \right\rangle\right|^2}{\varepsilon_n - \varepsilon_{n'}} \tag{3.578}$$

that it reduces to the matrix element $\left\langle n' \middle| \widehat{H}_1 \middle| n \right\rangle$ calculation, which develops as above to yield:

$$\begin{aligned}\left\langle n' \middle| \widehat{H}_1 \middle| n \right\rangle &= \frac{b}{2}\left\langle n' \middle| \hat{x}^2 \middle| n \right\rangle \\ &= \frac{b\alpha^2}{4}[\sqrt{(n+1)(n+2)}\underbrace{\langle n' | n+2\rangle}_{\delta_{n',n+2}} + n\underbrace{\langle n' | n\rangle}_{0} \\ &\quad + (n+1)\underbrace{\langle n' | n\rangle}_{0} + \sqrt{n(n-1)}\underbrace{\langle n' | n-2\rangle}_{\delta_{n',n-2}}]\end{aligned} \tag{3.579}$$

thus selecting only the non-vanishing states $n' = n+2$ and $n' = n-2$ for which we separately have:

$$\left|\left\langle n+2 \middle| \widehat{H}_1 \middle| n \right\rangle\right|^2 = \frac{b^2\alpha^4}{16}(n+1)(n+2) \tag{3.580}$$

$$\left|\left\langle n-2 \middle| \widehat{H}_1 \middle| n \right\rangle\right|^2 = \frac{b^2\alpha^4}{16}n(n-1) \tag{3.581}$$

Therefore we still need to evaluate the differences:

$$\varepsilon_n - \varepsilon_{n+w} = \hbar\omega_0\left(n+\frac{1}{2}\right) - \hbar\omega_0\left(n+w+\frac{1}{2}\right) = -\hbar\omega_0 w = \begin{cases} 2\hbar\omega_0 \ , w=-2 \\ -2\hbar\omega_0 \ , w=2 \end{cases} \tag{3.582}$$

so that the second order energy correction becomes:

$$\mathrm{E}_n^{(2)} = \frac{\left|\left\langle n-2 \middle| \widehat{H}_1 \middle| n \right\rangle\right|^2}{\varepsilon_n - \varepsilon_{n-2}} + \frac{\left|\left\langle n+2 \middle| \widehat{H}_1 \middle| n \right\rangle\right|^2}{\varepsilon_n - \varepsilon_{n+2}}$$

$$=\frac{b^2\alpha^4}{16}\left[\frac{n(n-2)}{2\hbar\omega_0}+\frac{(n+1)(n+2)}{-2\hbar\omega_0}\right]$$

$$=-\frac{b^2\alpha^4}{8\hbar\omega_0}\left(n+\frac{1}{2}\right)$$

$$=-\frac{b^2\alpha^4}{8\hbar^2\omega_0^2}\underbrace{\hbar\omega_0\left(n+\frac{1}{2}\right)}_{\varepsilon_n}=-\frac{b^2}{8\hbar^2\omega_0^2}\frac{\hbar^2}{m^2\omega_0^2}\varepsilon_n=-\frac{b^2}{8k_{\omega_0}^2}\varepsilon_n \tag{3.583}$$

with an identical overlap with the result of the series expansion, thus confirming once more the reliability of the perturbation and annihilation-creation algorithms.

2. When the perturbation over the harmonic motion is considered linear in coordinate, i.e., when

$$\widehat{H}_1=b\hat{x},\ b\in \mathrm{R} \tag{3.584}$$

the problem seems to be even more simpler under the total Hamiltonian influence

$$\widehat{H}=\widehat{H}_0+\widehat{H}_1=\frac{\hat{p}^2}{2m}+\frac{k_{\omega_0}}{2}\hat{x}^2+b\hat{x}$$

$$=\frac{\hat{p}^2}{2m}+\frac{k_{\omega_0}}{2}\left(\hat{x}^2+\frac{2b}{k_{\omega_0}}\right)$$

$$=\underbrace{\frac{\hat{p}^2}{2m}+\frac{k_{\omega_0}}{2}\Bigg(\underbrace{\hat{x}+\frac{b}{k_{\omega_0}}}_{\hat{x}^{\#}}\Bigg)^2}_{\widehat{H}_0^{\#}}-\frac{b^2}{2k_{\omega_0}}=\widehat{H}_0^{\#}-\frac{b^2}{2k_{\omega_0}} \tag{3.585}$$

however appearing the problem whether the new coordinate operator $\hat{x}^{\#}$ maintains the same commutation relationship with momentum, a crucial matter in preserving the unperturbed harmonic spectrum. One has:

$$\left[\hat{p},\hat{x}^{\#}\right]=\left[\hat{p},\hat{x}+\frac{b}{k_{\omega_0}}\right]=\underbrace{\left[\hat{p},\hat{x}\right]}_{-i\hbar}+\underbrace{\left[\hat{p},\frac{b}{k_{\omega_0}}\right]}_{0}=-i\hbar \tag{3.586}$$

thus assuring the maintenance of the harmonic spectrum even with the shifter coordinate unperturbed Hamiltonian,

$$\widehat{H}_0^{\#}|n\rangle=\varepsilon_n|n\rangle \tag{3.587}$$

while the perturbed spectra is obtained employing the energy eigen-value problem for the whole Hamiltonian:

$$\widehat{H}|n\rangle=\left(\widehat{H}_0^{\#}-\frac{b^2}{2k_{\omega_0}}\right)|n\rangle=\left(\varepsilon_n-\frac{b^2}{2k_{\omega_0}}\right)|n\rangle\overset{!}{=}\mathrm{E}_n|n\rangle \tag{3.588}$$

from where immediately follows:

$$\mathrm{E}_n=\varepsilon_n-\frac{b^2}{2k_{\omega_0}} \tag{3.589}$$

as the corrected energy of the harmonic oscillator with linear coordinate perturbation.

The only remaining point is the assessment of the order in which this correction appears, and this will be done through searching this result with the help of annihilation-creation approach. As such, for the first order correction we obtain:

$$\begin{aligned}
\mathrm{E}_n^{(1)}&=\langle n|\widehat{H}_1|n\rangle=b\langle n|\hat{x}|n\rangle=\frac{b\alpha}{\sqrt{2}}\langle n|\left(\hat{a}^{+}+\hat{a}\right)|n\rangle\\
&=\frac{b\alpha}{\sqrt{2}}[\langle n|\underbrace{\hat{a}^{+}|n\rangle}_{\sqrt{n+1}|n+1\rangle}+\langle n|\underbrace{\hat{a}|n\rangle}_{\sqrt{n}|n-1\rangle}]\\
&=\frac{b\alpha}{\sqrt{2}}[\sqrt{n+1}\underbrace{\langle n|n+1\rangle}_{0}+\sqrt{n}\underbrace{\langle n|n-1\rangle}_{0}];\\
\mathrm{E}_n^{(1)}&=0
\end{aligned} \tag{3.590}$$

For the second order we need the non-diagonal matrix elements of the above terms

$$\langle n'|\hat{x}|n\rangle = \frac{b\alpha}{\sqrt{2}}[\sqrt{n+1}\underbrace{\langle n'|n+1\rangle}_{\delta_{n',n+1}} + \sqrt{n}\underbrace{\langle n'|n-1\rangle}_{\delta_{n',n-1}}] \tag{3.591}$$

that select the proper states with $n' = n+1$ and $n' = n-1$, and, as in the previous analysis we found out:

$$\left|\langle n+1|\widehat{H}_1|n\rangle\right|^2 = \frac{b^2\alpha^2}{2}(n+1) \tag{3.592}$$

$$\left|\langle n-1|\widehat{H}_1|n\rangle\right|^2 = \frac{b^2\alpha^2}{2}n \tag{3.593}$$

$$\varepsilon_n - \varepsilon_{n+w} = -\hbar\omega_0 w = \begin{cases} \hbar\omega_0 \ , \ w = -1 \\ -\hbar\omega_0 \ , \ w = 1 \end{cases} \tag{3.594}$$

so that we write

$$\begin{aligned} E_n^{(2)} &= \frac{\left|\langle n-1|\widehat{H}_1|n\rangle\right|^2}{\varepsilon_n - \varepsilon_{n-1}} + \frac{\left|\langle n+1|\widehat{H}_1|n\rangle\right|^2}{\varepsilon_n - \varepsilon_{n+1}} \\ &= \frac{b^2\alpha^2}{2}\left[\frac{n}{\hbar\omega_0} - \frac{n+1}{\hbar\omega_0}\right] = -\frac{b^2\alpha^2}{2}\frac{1}{\hbar\omega_0} = -\frac{b^2}{2\hbar\omega_0}\frac{\hbar}{m\omega_0} = -\frac{b^2}{2k_{\omega_0}} \end{aligned} \tag{3.595}$$

thus identifying the present correction as being that of the second order.

We let for the reader to practice the similar perturbation problems in momentum, with the perturbation Hamiltonian taking the forms $\widehat{H}_1 = \left\{b\hat{p}^2, b\hat{p}^4, b\hat{p}\hat{x}^2\hat{p}\right\}$, $b \in \mathrm{R}$, chosen so that to be hermitic, by using the annihilation-creation representation for the momentum operator and the associate rules.

3.7.5 QUASI-FREE ELECTRONIC MODEL OF SOLIDS

As we saw previously, see Sections 3.3.3, 3.4.3, and 3.5.3, in the solid state environment there seems to exists two equivalent types of wave-function