Quantum Chemistry by Levine

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1 Chapter 9 Perturbation Theory

9.1
$\hat{H} = \hat{H}^0 + \hat{H}^,$
$\hat{H}^0 = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$
$\hat{H} = C$
$E^1 =< \phi|C|\phi >= C$

9.2
(a)$E^2 = \Sigma_{m!=n}|H^,_{mn}|^2/(E^0_n - E^0_m)$
where $H^,_{mn} =< \phi_m|H^,|\phi_n >= C < \phi_m|\phi_n >= 0$
So $E^2 = 0$
there is no second order correction. One order correction is already precise.

(b) $\Psi^1 = \Sigma_{m!=n}\frac{<\Psi^0_m|H^,|\Psi^0_n>}{E^0_n - E^0_m}\Psi^0_m$
where $< \Psi^0_m|H^,|\Psi^0_n >= 0$
So $\Psi^{(1)} = 0$

(c)$\hat{H}\Psi = E\Psi$

9.3
$E^{(1)} =< \Psi_n|H^,|\Psi >= \sqrt{\frac{4\alpha^3}{\pi}}\int_{-\infty}^{\infty} x^2 e^{-\alpha x}(cx^3 + dx^4)dx = \frac{15d\hbar^2}{16\pi^2 v^2 m}$

9.4
$E^{(1)} =< \Psi^0_n|H^,|\Psi^0_n >= \frac{2}{l}\int_{l/4}^{3l/4} V_0 sin^2(\frac{n\pi x}{l})dx$
where $V_0 = \frac{\hbar^2}{ml^2}$

for $n = 1$:
$E^0_1 = \frac{h^2}{8ml^2}$
$E^{(1)}_1 = 0.818\frac{\hbar^2}{ml^2}$

So correction $E = E_1^{(0)} + E_1^{(1)} = 5.75\frac{\hbar^2}{ml^2}$
for $n = 2$:
$E_2^{(0)} = \frac{4h^2}{8ml^2}$
$E_2^{(1)} = \frac{\hbar^2}{2ml^2}$
So correction $E = E_2^{(0)} + E_2^{(1)} = 20.23\frac{\hbar^2}{ml^2}$

9.5

it is closest to the waveform

9.6

$\Psi_n^{(1)} = \Sigma_{m!=n} a_m \Psi_m^{(0)} = \sqrt{\frac{2}{l}}\Sigma_{m!=n} a_m sin(\frac{m\pi x}{l})$
in the previous question, we know that:
$a_m =< \Psi_m^{(0)}|H'|\Psi_n^{(0)} >= \frac{2}{l}\int_{l/4}^{3l/4} V_0 sin(\frac{n\pi x}{l}) sin(\frac{m\pi x}{l})$

9.7

(a)$< \Psi_m^{(0)}|H'|\Psi_n^{(0)} >$ for $n = 1$ and m is even
So $\Psi_n^{(0)}$ is an even function and $\Psi_m^{(0)}$ is odd function
the integral is 0