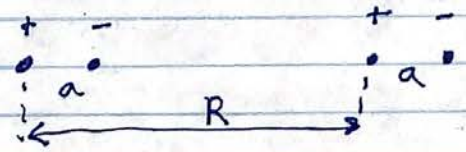
HW #6, chem 2430 Answers

1.

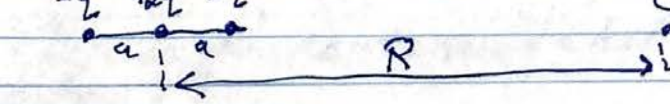


$$V = \frac{q^2}{R} - \frac{q^2}{R-a} - \frac{q^2}{R+a} + \frac{q^2}{R}$$

$$= \frac{2q^2}{R} - \frac{q^2}{R}\left(1 + \frac{a}{R} + \frac{a^2}{R^2} + \dots\right) - \frac{q^2}{R}\left(1 - \frac{a}{R} + \frac{a^2}{R^2} + \dots\right)$$

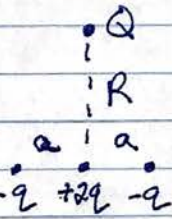
$$= -\frac{2q^2a^2}{R^3} = \frac{-2\mu\cdot\mu}{R^3}$$

2.



$$V = \frac{2qQ}{R} - \frac{qQ}{R+a} - \frac{qQ}{R-a} \approx \frac{-2Qqa^2}{R^3}$$

quadrupole moment $= -2qa^2$



$$V = \frac{2qQ}{R} - \frac{qQ}{\sqrt{R^2+a^2}} - \frac{qQ}{\sqrt{R^2+a^2}}$$

$$= \frac{2qQ}{R} - \frac{2qQ}{R}\left[1 - \frac{a^2}{2R^2}\right] = \frac{qQa^2}{R^3}$$

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3. For the points that I chose, I got the following fits

1 GTO $\quad 0.86\, e^{-0.72r^2}$

2 GTO's $\quad 0.46\, e^{-6.28r^2} + 0.52\, e^{-0.33r^2}$

3 GTO's $\quad 0.26\, e^{-19.3r^2} + 0.41\, e^{-1.33r^2} + 0.32\, e^{-0.22r^2}$

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4. $V = \frac{1}{2}kx_1^2 + \frac{1}{2}kx_2^2 + \gamma x_1 x_2$

$$\left.\begin{array}{l} \chi_1 = 1/\sqrt{2}\,(x_1 + x_2) \\ \chi_2 = 1/\sqrt{2}\,(x_1 - x_2) \end{array}\right\} \rightarrow \begin{array}{l} x_1 = 1/\sqrt{2}\,(\chi_1 + \chi_2) \\ x_2 = 1/\sqrt{2}\,(\chi_1 - \chi_2) \end{array}$$

$$V = \frac{1}{2}k\chi_1^2 + \frac{1}{2}k\chi_2^2 + \frac{\gamma}{2}(\chi_1^2 - \chi_2^2)$$

$$= \frac{1}{2}(k+\gamma)\chi_1^2 + \frac{1}{2}(k-\gamma)\chi_2^2$$

Separates!

$$\omega_1' = \sqrt{(k+\gamma)/\mu} \qquad \omega_2' = \sqrt{(k-\gamma)/\mu}$$

$$\omega_1' = \sqrt{\frac{k}{\mu}}\sqrt{1+\gamma/k} = \omega_0\left(1+\frac{\gamma}{2k}-\frac{\gamma^2}{8k^2}+\dots\right)$$

$$\omega_2' = \sqrt{k/\mu}\sqrt{1-\gamma/k} = \omega_0\left(1-\frac{\gamma}{2k}-\frac{\gamma^2}{8k^2}-\dots\right)$$

$$\omega_1'+\omega_2' = 2\omega_0 - \frac{\gamma^2\omega_0}{4k^2}$$

The change in the zero-point energy due to the interaction is

$$\frac{1}{2}\left[\omega_1'+\omega_2'-2\omega_0\right] = -\frac{\gamma^2\omega_0}{4k^2}$$

This is the same result that we got from 2nd order PT.