Why the Particle-in-a-Box Model Works Well for Cyanine Dyes but Not for Conjugated Polyenes

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It is vital to discuss the particle-in-a-box (PB) model in quantum theory sections of undergraduate chemistry classes because of its simplicity. It affords most of the features of real quantum systems such as quantized energy levels, zero-point energy, and Heisenberg uncertainty. The PB Schrödinger equation is easy to solve. Despite its highly approximate character the PB model is useful in describing the properties of real quantum systems. For instance, some authors have recently advocated for using the PB model to describe the properties of semiconducting nanocrystals to emphasize the relevance of quantum theory "in the context of real scientific, societal, and technological problems" *(1)*. Another example is the recently published physical chemistry textbook by Engel *(2)* that features a chapter on applications of the PB model.

One of the educationally most illustrative chemical applications of the one-dimensional PB model is the modeling of the π-to-π* excitations in conjugated chain molecules. Spectroscopy experiments that make use of the PB model have been described in popular physical chemistry laboratory textbooks *(3, 4)* and in this *Journal (5–8)*. These articles and books are also an excellent source for data that can be used for homework assignments in physical chemistry courses. One can easily calculate the wavelength, λ, corresponding to the energy gap between the highest occupied molecular orbital (HOMO) π and the lowest unoccupied molecular orbital (LUMO) π* level from the PB model. The only adjustable parameter is the box length, L. This model can be successfully applied to cyanine dyes. With a suitably chosen expression for L the results obtained from an unmodified one-dimensional PB model are within a few percent of the experimentally observed longest UV–vis absorption wavelength maxima, λ_{max}.

The symmetric cyanine dyes **1** are given by the formula

1
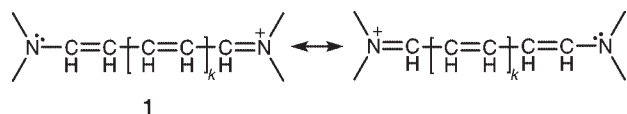
with $k = 0, 1, 2, 3, ...$ and a total of $m = 2k + 5$ atoms in the conjugated chain backbone (including the nitrogen atoms). The number of π-electron pairs equals $k + 3$. The spectra of other types of cyanine dyes, which have been discussed extensively in the literature *(9–11)*, can be represented by the simplified general formula
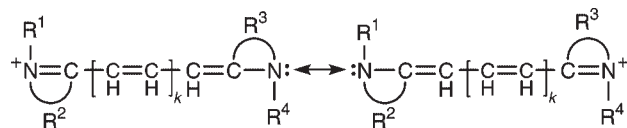
An example is the family of thiacarbocyanine dyes

2
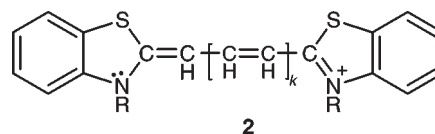
Cyanine Dyes: Unmodified PB Model and Comparison with Experimental Data

In the cyanine dyes the delocalization of the π system is so strong that there is very little bond-length alternation along the conjugated chain *(11)*. Let us assume that for the cyanines **1** all C−C bond lengths equal roughly 144 pm, which is the average of the C−C bond distances in ethane and ethene. Assuming further an all-trans zigzag carbon chain with C−C−C bond angles of 120°, we obtain a linear dimension, a, of 249 pm for each −CH=CH− unit (249 = 144 × √3). Some extra space is needed to accommodate the two terminating −NR$_2$ groups and one more =CH− group. A reasonable value for the extra space, b, might be on the order of 500 to 600 pm. We choose a value of $b = 567$ pm, which leads to overall best agreement between calculated and experimental data for **1** and is also the right magnitude to obtain a box size that corresponds closely to the linear dimension of the conjugated chain. We have therefore $L = a(k + 1) + b = [249(k + 1) + 567]$ pm for the symmetric cyanines **1**. For other series of cyanine dyes, the parameter b might need to be adjusted to account for polarizable groups at the chain ends *(6, 7, 10)*. The PB energy levels for an electron in a "box" of length L are given as

$$E_n = \frac{h^2 n^2}{8 m_e L^2}; \quad n = 1, 2, 3, ... \quad (1)$$

where n is the quantum number, m_e is the electron mass, and h is Planck's constant. The wave function for each energy level is given as

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right) \quad (2)$$

By calculating the difference between the HOMO and LUMO levels from eq 1 as a function of k and converting to wavelengths one obtains results for λ_{max} that are close to the experimental data. A comparison of calculated and experimental absorption wavelengths is found in Table 1.[1] An energy level diagram for the particle in a box as a function of L is shown in Figure 1. Since $n_{HOMO} \propto L$ (the longer the chain the more electrons we have) and $E_n \propto (n/L)^2$ the HOMO

Table 1. Calculated and Observed Longest Absorption Wavelengths, λ_{max}, for Symmetric Cyanines

k	n_{HOMO}	λ_{max}/nm	
		Calc	Exp
0	3	314	313
1	4	416	416
2	5	518	519
3	6	621	625

NOTE: Calculations based on the PB model with a box length of $L = [249(k + 1) + 567]$ pm. Experimental data taken from ref 11.

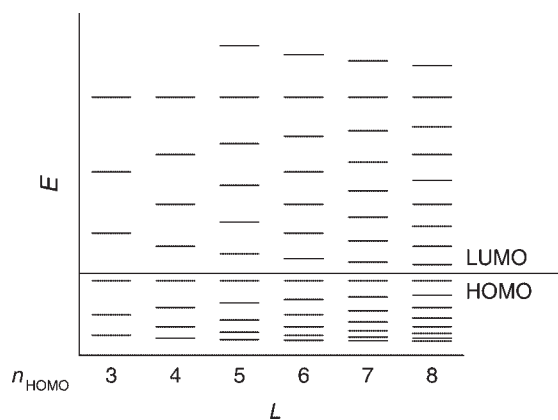Figure 1. PB energy levels as a function of chain length, L. Shown here is an example where for the smallest L the HOMO level is $n = 3$. The HOMO–LUMO energy gap is inversely proportional to the increase in L.

level stays constant as the conjugated chain grows. At the same time, the LUMO energy level drops in energy relative to the HOMO. The energy gap ΔE is proportional to $1/L$. Therefore, $\lambda_{max} \propto L$, which is confirmed by the experimental data.

Students frequently become suspicious—and for good reasons—about this excellent performance of the model, in particular when confronted with the error bars of first-principles theoretical methods to calculate excitation wavelengths (for instance methods based on time-dependent density functional theory, ref 12). For a highly simplified model such as PB, it is important that the student realizes how various approximations can cause a model to perform poorly in numerical predictions while still capturing the essence of "what is going on in the system". Conversely, as it is the situation here, the student needs to understand why a model may yield good agreement with experimental data despite its crude nature.

Cyanine Dyes: A Refined PB Model

One of the approximations that is made when the PB model is applied to treat the π orbitals of cyanines is that the potential $V(x)$ is assumed to be constant over the length $0 \le x \le L$ of the box. In reality, however, there will be variations of the potential even for the relatively loosely bound π orbitals. Such variations in the potential should reflect the position of the atoms in the molecule (Figure 2). Consequently, one may wonder why the PB model works for describing the π to π* excitations in cyanines because the potential is not constant along the chain.

By using first-order perturbation theory an argument may be developed in class or given as a homework problem that rationalizes the success of the PB model for calculating the λ_{max} for cyanine dyes. Basic quantum theory lectures often discuss the first-order correction to the energy levels of a quantum system caused by the presence of a perturbation of the potential energy.[2] Let the perturbing potential of the PB potential be $V'(x)$, then the first-order correction to the energy of each level E_n of eq 1 is

$$E_n' = \int_0^L \psi_n^*(x) V'(x) \psi_n(x)\,dx \qquad (3)$$

For $V'(x)$ we assume, approximately, a cosine term with a number of peaks and troughs such as the one shown in
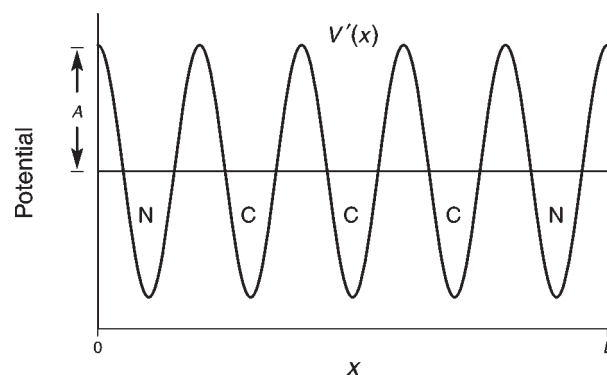

Figure 2. Perturbation of the potential along a conjugated chain without bond-length alternation. The unperturbed PB potential is shown with the horizontal line and A is defined in eq 4. Shown here is an example for a cyanine with $k = 0$, i.e., for a chain of $m = 5$ atoms and 3 occupied π orbitals.

Figure 2. There is a trough for each atom along the conjugated chain backbone and a peak in between the atoms and beyond the terminating atoms of the chain. This shape of the potential reflects the presence of an effective (shielded) nuclear attraction in the vicinity of the atomic cores, the electronic repulsion within the delocalized π bonds, and the less attractive potential beyond the terminating atoms along the chain axis. The potential

$$V'(x) = A \cos\left(\frac{2m\pi}{L} x\right) \qquad (4)$$

affords the required $m = 2k + 5$ troughs along the chain for a number of m atoms in the chain backbone. The factor A represents the strength of the perturbation. For the perturbing potential it is not essential that the peaks and troughs have the same magnitude to obtain a vanishing first-order energy correction. For instance, one could simply add a constant to $V'(x)$ to adjust the ratio of peak and trough magnitudes with-

out further changing the difference between the energy levels and the results for the $\lambda_{\max}$.

Both $\psi^*\psi$ and V' are of even symmetry; therefore the E_n do not trivially vanish. The rule for odd integrands cannot be applied here. By using eq 3 with $V'(x)$ from eq 4 and the wave functions from eq 2 one obtains

$$E_n' = \frac{A\,n^2}{\pi}\frac{\cos(m\pi)\sin(m\pi)}{mn^2 - m^3} = \frac{A\,n^2}{2\pi}\frac{\sin(2m\pi)}{mn^2 - m^3}$$

$$= \frac{A}{4\pi}\left\{\frac{2\sin(2m\pi)}{m} - \frac{\sin\left[2\,(m-n)\pi\right]}{m-n}\right.$$

$$\left. - \frac{\sin\left[2\,(m+n)\pi\right]}{m+n}\right\} \quad (5)$$

Equation 5 nonetheless yields zero (unless $m = n$) because of the sin(integer × π) = 0 terms. Students can obtain this result easily with a computer algebra software program such as Mathematica (13) or Maple (14), in a more traditional way by using integral tables (15), or by converting trigonometric into exponential functions and integrating each term. Equation 5 lists various forms of the integral that might be obtained, depending on the strategy used to obtain the solution.[3] The HOMO level has a quantum number $n_{\mathrm{HOMO}} = k + 3$, the LUMO has $n_{\mathrm{LUMO}} = k + 4$. Neither is equal to $m = 2k + 5 = 2n_{\mathrm{HOMO}} - 1$; therefore terms in eq 5 with a zero denominator for $m = n$ are not of concern for the longest wavelength absorption.

The fact that the first-order perturbation energies in this refined PB model are zero helps rationalizing why the unmodified PB model yields such good agreement with experimental values for the lowest excitation energies for the cyanine dyes. The agreement is achieved despite the fact that the potential is not expected to be really constant along the chain axis. However, if one assumes a periodic potential with a small amplitude such as the one shown in Figure 2, which is a reasonable approximation for the delocalized π system in cyanines where little bond-length alternation occurs, the calculated excitation wavelengths are to first order the same as in the unmodified PB model. For a strong perturbation, the second and higher-order energy corrections should not be neglected. We note in passing that a similar result can be obtained for the hindered rigid rotor (which, for example, might be used to describe the energy levels of a rotating methyl group in an organic molecule). The model is also applicable to the π orbitals of conjugated cyclic chains (benzene, cyclopentadienyl anion, and other annulenes) with similar implications regarding the first-order perturbed energy levels. In fact, the linear or cyclic PB model offers close similarities to the Hückel model that has been so successful in chemistry: the Hückel molecular orbital coefficient for orbital number n at the mth site of a chain or loop of atoms is proportional to the amplitude of the corresponding PB wave function at the site position for a linear or cyclic box of the same extension. The PB can further be extended to other types of conjugated species (see ref 16 for further details).
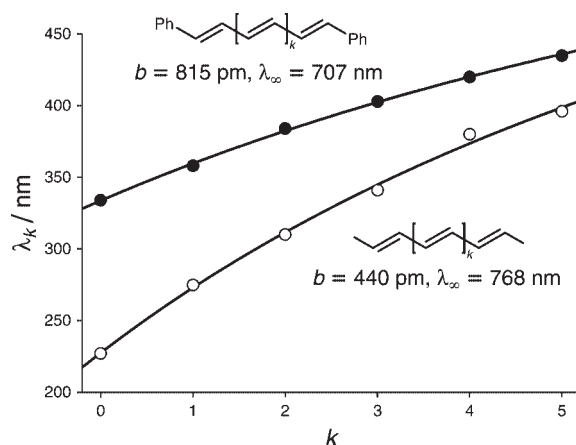

Figure 3. Longest absorption wavelength of polyenes as a function of chain length. Ph = phenyl. Experimental wavelengths $\lambda_{\max}$ taken from ref 17, Table 2.2. The lines are fits according to a modified PB model that accounts for bond-length alternation, see Table 2.

Treatment of Polyenes with the Refined PB Model: Effect of Bond-Length Alternation

For cyanine dyes of different chain lengths an approximately constant spacing of the $\lambda_{\max}$ on the wavelength scale is found experimentally (see Table 1). This means that their colors cover the whole visible spectrum and beyond. Polyenes, on the other hand, have a different behavior of $\lambda_{\max}$ as a function of chain length. The $\lambda_{\max}$ of polyenes converge from short wavelengths to a finite wavelength limit λ_∞ as the chain grows (11, 17), not to the limit $\lambda \to \infty$ as in the case of the cyanine dyes. Two examples of polyenes are shown in Figure 3. Therefore, red colors typically are observed for long conjugated polyene chain backbone molecules (11) such as β-carotene (orange, $n_{\mathrm{HOMO}} = 11$, $\lambda_{\max} = 453$ nm) (18) or lycopene (below)
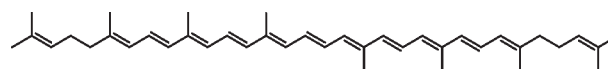
(dark red, $n_{\mathrm{HOMO}} = 11$, $\lambda_{\max} = 472$ nm) (18), which are responsible for the color of carrots and tomatoes, respectively.

In terms of the excitation energy ΔE, the cyanines afford $\Delta E \propto 1/L$ and the infinite chain-length absorption wavelength λ_∞ is infinity. For long-chain polyenes, on the other hand, a finite λ_∞ is observed, which means $\Delta E \to$ constant for an infinite conjugated polyene chain. We will show that this behavior can be described straightforwardly with the modified PB model developed in the last section by considering the bond-length alternation in polyenes. For a detailed analysis of this situation see, for example, ref 10.

Polyenes have a significant bond-length alternation because the bonds cannot be represented as both single and double bonds in equivalent resonance structures as, for example, the cyanines 1. For a polyene with an even number
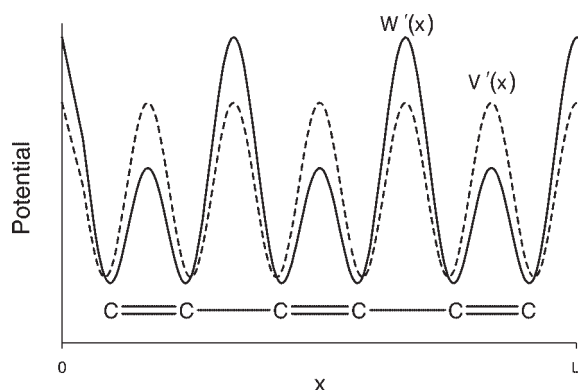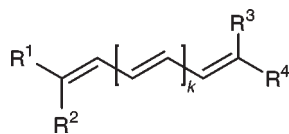
Figure 4. Perturbation of the potential along a conjugated chain with bond-length alternation. Shown here as an example is the model potential $W'(x)$ of eq 6 for a polyene with $k = 1$, i.e., for a chain of $m = 6$ atoms and 3π occupied orbitals. For comparison, the potential $V'(x)$ without bond-length alternation is also shown.

Figure 5. Perturbed PB energy levels $E_n + E_n'$ as a function of L. Shown here is an example where for the smallest L the HOMO level is $n = 3$. The box is perturbed by the potential $W'(x)$. The dashed lines indicate the few *unperturbed* PB levels that do not coincide with those of the perturbed PB model.

$m = 2k + 4$ carbon atoms in the conjugated chain

we have $n_{HOMO} = k + 2 = m/2$, which is equal to the number of conjugated double bonds, and $n_{LUMO} = (m/2) + 1$. We adopt the modified (perturbed) PB model of the last section. To account for the bond-length alternation we add a *second* perturbing potential to $V'(x)$ and obtain

$$W'(x) = A\cos\left(\frac{2m\pi}{L}x\right) + B\cos\left(\frac{m\pi}{L}x\right) \qquad (6)$$

where the factors A and B represent the strengths of the perturbations. Figure 4 shows the modified potential and demonstrates that it accounts for a certain degree of bond-length alternation for C=C double and C—C single bonds.

To evaluate the effect on the PB energy levels one needs to calculate

$$E_n' = \int_0^L \psi_n^*(x)\,W'(x)\,\psi_n(x)\,dx \qquad (7)$$

The term proportional to A in E_n' yields zero for the HOMO and LUMO levels just as was found for the cyanines. The term proportional to B is readily obtained from eq 5 simply with A replaced with B and m with $m' = m/2$. However, for the polyene chain $n_{HOMO} = m' = m/2$, too. Therefore we need to consider the behavior of eq 5 for the case that $n = m' = m/2$.

The expression for E_n' is not zero if $n = m'$. In this case eq 5 contains indeterminate terms (0/0). The correct value for the limit $n \rightarrow m'$ can be obtained, for example, by momentarily considering n and m as continuous variables and
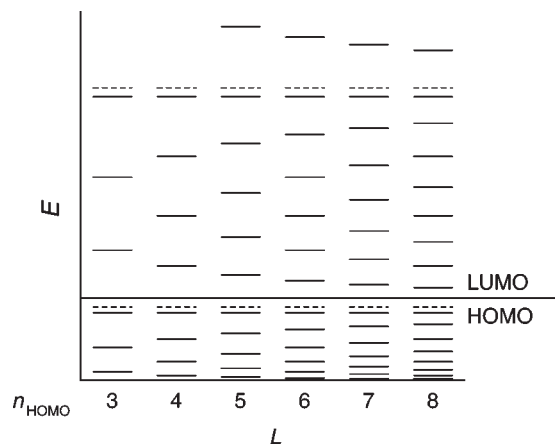
using the l'Hospital rule. Differentiating the numerator and denominator in eq 5 separately with respect to m, replacing A with B and m with m', and letting $m' = 1, 2, 3, \ldots$ again afterwards, yields

$$\lim_{n \rightarrow m'} E_n' = -\frac{B}{2}\cos\left(2m'\pi\right) = -\frac{B}{2} \qquad (8)$$

Alternatively, we can set $n = m/2$ before the integration in eq 7 and obtain straightforwardly from an integral table or a computer algebra program for the term proportional to B

$$E_{n=m/2}' = -\frac{B}{2}\frac{2m\pi - 4\sin(m\pi) + \sin(2m\pi)}{2m\pi}$$
$$= -\frac{B}{2} \qquad (9)$$

for integer m. In either case a constant shift of the HOMO level by an energy of $-B/2$ is obtained for the modified PB model with bond-length alternation. The reason for the lowering of the HOMO level is that its density $\psi^*\psi$ has the same periodicity as the bond-length alternation. For the other wave functions, the oscillations of the density around the perturbation cancel out in the integral that is used to calculate E'.[4]

As was shown above, for the cyanine dyes the case $n = m$ affects neither the HOMO nor the LUMO levels and is therefore not of concern for their longest-wavelength absorption. However, for the polyenes the additional perturbing potential that describes the bond-length alternation lowers the energy of the HOMO by a constant magnitude, $B/2$, independent of the chain length. The LUMO level is not affected. This situation is depicted in Figure 5. The HOMO levels are lowered owing to the presence of the $B\cos[(m\pi/L)x]$ term in W'. Higher unoccupied levels with $n = 2n_{HOMO}$ are changed owing to the presence of the $A\cos[(2m\pi/L)x]$ term in W'.

Table 2. Calculated and Observed Longest Absorption Wavelengths, λ_{max}, for Conjugated Polyenes

k	n_{HOMO}	λ_{max}/nm CH$_3$(CH=CH)$_k$CH$_3$		λ_{max}/nm Ph(CH=CH)$_k$Ph	
		Calc	Exp	Calc	Exp
0	2	227	227	334	334
1	3	273	275	360	358
2	4	312	310	382	384
3	5	345	341	402	403
4	6	374	380	420	420
5	7	399	396	436	435
9	11	474		485	
13	15	524		519	

NOTE: Calculations based on a fit of the experimental data to a modified PB model considering bond-length alternation. Fitted box parameters b for $L = [245(k + 2) + b]$ pm and limiting wavelengths λ_{∞} in nm (i.e., $B/2$ converted to wavelengths, see text) are listed in Figure 3. Experimental data taken from ref 17.

As the conjugated polyene chain grows, the HOMO–LUMO energy gap corrected by first-order terms converges to $B/2$ (instead of zero for the cyanine dyes). As mentioned previously, for long-chain polyenes $\Delta E \rightarrow$ constant as the chain grows to infinite length. According to the modified PB model, the occurrence of such a limit is caused by the bond-length alternation, which has a profound effect on the energy of the HOMO. The numerical value of the ΔE limit for very long polyene chains corresponds to our parameter $B/2$. Its value represents, upon conversion to wavelengths (see the Supplemental Material[ш]), the limiting absorption wavelength λ_{∞} that is found experimentally for long-chain polyenes.

The experimental absorption wavelengths for two series of conjugated polyenes are listed in Table 2. We have performed a least-squares fit of the excitation energies (converted from the experimental wavelengths) to the HOMO–LUMO gap of the modified PB with bond-length alternation. The same parameter of 249 pm for each $-CH_2=CH_2-$ increment has been used as previously determined for the cyanine dyes. That is, the fit had two adjustable parameters: b for the box length L in eq 1 (see footnote of Table 2) and the limiting value $B/2$ for infinite chain length. The software Gnuplot (19) was used for the fitting procedure. After conversion of $B/2$ back to the wavelength for infinite chain length, λ_{∞}, the fit yielded $b = 440$ pm, $\lambda_{\infty} = 768$ nm for CH$_3$(CH=CH)$_k$CH$_3$, and $b = 815$ pm, $\lambda_{\infty} = 707$ nm for Ph(CH=CH)$_k$Ph. The B parameters are 3.23 eV and 3.51 eV, respectively. Since the b parameter describes how far the "box" extends into the side chains, it is, as expected, significantly larger for the systems with the phenyl substituents. The orbitals of the conjugated chains are to some extent delocalized over the phenyl rings, which causes this increase in the effective box size as compared to the other systems. The limiting wavelengths for infinite chain lengths are perhaps larger than one might expect from just looking at Figure 3 because of the rather slowly decreasing HOMO–LUMO gap as a function of chain length [proportional to $1/(L + \text{constant})$]. As seen from the plot, the agreement between the modified PB prediction and the experimental data is of similar quality as found previously for the cyanine dyes. Table 2 contains the calculated absorption wavelengths as a function of chain length corresponding to the fit parameters. The Microsoft Excel spreadsheet (see the Supplemental Material[ш]) used to calculate the wavelengths for cyanine dyes was also used for calculations of these wavelengths.

It is seen that λ_{∞} may vary on the order of 50 nm between different families of polyenes depending on the terminating groups. For an $n_{HOMO} = 11$ system both models predict a wavelength close to 474 nm, which is in good agreement with the experimental absorption wavelength for lycopene (472 nm). As another example, consider the chemical formula for lycopene: eliminating H$_2$ from each of the single-bond C−C units at both ends of the conjugated subchain in lycopene gains *four* more double bonds; that is, we have a conjugated chain with $n_{HOMO} = 15$. For an $n_{HOMO} = 15$ system, the predicted wavelengths for our two parameter sets are 524 and 519 nm, respectively. Kuhn quoted an absorption wavelength of 504 nm for dehydro-lycopene (10), which, again, is in good agreement with the predictions of the modified PB model. Students should be reminded that a deviation at larger wavelength represents less of an error in terms of energy (e.g., 100 nm–101 nm corresponds to a difference of 0.1 eV, 504 nm–524 nm corresponds to a difference of 0.1 eV as well).

Conclusions

The PB model works well for cyanine dyes and other conjugated linear systems with little or no bond-length alternation not because a realistic box potential is really "flat", but because the periodicity in the potential does not affect the HOMO–LUMO gap to first order. This fact can be illustrated by first-order perturbation theory. For systems with significant bond-length alternation, the unmodified PB model is not able to describe the finite absorption wavelength limit for infinite chains. However, by including a first-order perturbation of the potential that has the periodicity of the bond-length alternation this observation can be modeled straightforwardly.

Acknowledgments

ᵚSupplemental Material

A Microsoft Excel spreadsheet used to generate the calculated data in Table 1 and the conversion factors between energy and wavelength of light used in the spreadsheet are available in this issue of *JCE Online*.

Notes

1. A Microsoft Excel spreadsheet, available in the Supplemental Material[W], takes the box parameters a and b as input and calculates λ_{max} as a function of k. The spreadsheet was used to generate the calculated data in Table 1 using the conversion factors listed in the Appendix, which is also in the Supplemental Material.[W]

2. It is not essential to use formal perturbation theory to take advantage of the argument. Assuming that the students are familiar with the expression for the expectation value for an observable X, i.e., $\langle X \rangle = \int d\tau\, \psi^* \hat{X} \psi$, eq 3 can simply be introduced as the expectation value of the potential $V'(x)$ for the state described by quantum number n. The instructor can then mention that because $V'(x)$ contributes to the energy it should really have been included in the Hamiltonian in the first place. This would have led to wave functions that differ slightly from the PB wave functions. Because of the stationarity property of the eigenvalues of differential equations with boundaries, the respective energy modification due to the changes in the wave functions will be of small secondary order. The concept of a perturbation series expansion of the energy and the wave functions is implicitly present in this explanation without the need for explicitly developing the formalism in class.

3. The integral can be simplified first by applying a variable substitution $y = (\pi/L)x$ in which case one obtains

$$E_n \;=\; \frac{2A}{\pi}\int_0^\pi \sin^2(ny)\,\cos(2my)\,dy$$

4. A perturbing potential proportional to $\cos[(m\pi/L)x]$ affects PB energy levels with $n = m/2$ for which the electron density $\psi^*\psi$ has the same periodicity as the perturbing potential. A similar effect is known in band structure theory where the free electron levels of a one-dimensional lattice are perturbed near the Brillouin zone boundaries by the periodic potential. It is typical for integrals with sine and cosine functions that nonzero values are only obtained for proper matching periodicities.

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