Overlap Effects on Benzene Transmission

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1 Abstract

The Hückel molecular-orbital method (with overlap $S$) is used to derive the $S$-
modified version of the renormalization equations, which are then employed to
introduce overlap into the para-, meta- and ortho-benzene dimers' parameters.
Invoking the Lippmann-Schwinger scattering theory enables the spectral energy
transmission function $T(E)$ to be found for each of the benzene types. The ef-
flect of overlap on the behaviour of the various $T(E)$ curves is, indeed, marked,
even for low values of $S$, where all the curves’ symmetries become permanently
broken. As $S$ increases, the graphs become more distorted and suffer displace-
ments to lower energies. These results are so significant that they justify the
inclusion of overlap in all $T(E)$ studies of benzene.

2 Introduction

Benzene is one of the most important organic molecules, because of its structural
simplicity and its presence as a constituent of larger compounds. Consequently,
the molecule’s various properties have been extensively studied, over the years.
In particular, its electron transport properties are of interest [1], as being funda-
mental to the study of molecular wires, of various configurations and with
differing components.

Although the Hückel molecular-orbital method [2] has contained the overlap
integral $S$, since its earliest inception in the last century, overlap is quite often
overlooked in quantum calculations, when its magnitude is deemed so small, as
to render its inclusion unnecessary. A case in point arises in benzene transmis-
sion studies, where, because overlap has been considered negligible, it has so far
not appeared in any reports (see, e.g., [3]). Here, we redress this situation, by introducing overlap into the rescaling treatment of these molecules, and discover that overlap does, in fact, play a major role in determining the behaviour of the energy spectrum of the benzene transmission probability function $T(E)$.

The discrete Schrödinger equation gives rise to the rescaling technique [4], in which certain atomic sites are decimated, accompanied by renormalization of the parameters of the surviving sites. By this recursive process, the para-, meta- and ortho-benzenes can be mapped onto equivalent dimer molecules [5]. Such an approach facilitates the application of the Lippmann-Schwinger scattering theory [6] for calculating the transmission-energy spectral function $T(E)$ of the renormalized benzene molecules, thereby gaining insight into their electronic structure. In this paper, the rescaling method is extended, in a straightforward manner, to include overlap, allowing its significant effect on the three benzene types to be explored.

### 3 Rescaling Technique including Overlap

The molecular-orbital method is applied to a linear atomic chain (see Figure 1(a)), with Coulomb integral $\alpha_n$ at site $n$, bond integrals $\beta_{n-1,n}$ and $\beta_{n,n+1}$ with neighbouring sites $n-1$ and $n+1$, respectively, and corresponding overlap integrals $S_{n-1,n}$ and $S_{n,n+1}$. The discretized version of the Schrödinger equation leads to the familiar secular equations [2], of which those involving site $n$ are:

$$(E - \alpha_{n-1})c_{n-1} = (\beta_{n-2,n-1} - ES_{n-2,n-1})c_{n-2} + (\beta_{n-1,n} - ES_{n-1,n})c_n, \quad (1)$$

Figure 1: (a) Chain in initial configuration. (b) Rescaled chain, with site $n$ decimated and and sites $n \pm 1$ renormalized. Other sites (with parameters not shown) remain unchanged by the process.
\[(E - \alpha_n)c_n = (\beta_{n-1,n} - ES_{n-1,n})c_{n-1} + (\beta_{n,n+1} - ES_{n,n+1})c_{n+1}, \quad (2)\]
\[(E - \alpha_{n+1})c_{n+1} = (\beta_{n,n+1} - ES_{n,n+1})c_n + (\beta_{n+1,n+2} - ES_{n+1,n+2})c_{n+2}. \quad (3)\]

In order to eliminate site \(n\) from the set, we solve (2) for \(c_n\), and substitute into (1) (and similarly into (3)), resulting in
\[(E - \alpha_{n-1})c_{n-1} = (\beta_{n-2,n-1} - ES_{n-2,n-1})c_{n-2} + (\beta_{n-1,n} - ES_{n-1,n})c_n \times \left(\frac{\beta_{n-1,n} - ES_{n-1,n}}{E - \alpha_n} c_{n-1} + \frac{\beta_{n,n+1} - ES_{n,n+1}}{E - \alpha_n} c_{n+1}\right), \quad (4)\]

which can be rearranged as
\[
\left[E - \alpha_{n-1} - \frac{(\beta_{n-1,n} - ES_{n-1,n})^2}{E - \alpha_n}\right]c_{n-1} = (\beta_{n-2,n-1} - ES_{n-2,n-1})c_{n-2} + \frac{\beta_{n-1,n} - ES_{n-1,n}}{E - \alpha_n}(\beta_{n,n+1} - ES_{n,n+1})c_{n+1}. \quad (5)\]

Equation (5) can now be written in rescaled form as
\[(E - \tilde{\alpha}_{n-1})c_{n-1} = (\tilde{\beta}_{n-2,n-1} - ES_{n-2,n-1})c_{n-2} + (\tilde{\beta}_{n-1,n+1} - ES_{n-1,n+1})c_{n+1}, \quad (6)\]

where the renormalized parameters are
\[\tilde{\alpha}_{n-1} = \alpha_{n-1} + \frac{(\beta_{n-1,n} - ES_{n-1,n})^2}{E - \alpha_n}, \quad (7)\]
\[\tilde{\beta}_{n-1,n+1} = \frac{(\beta_{n-1,n} - ES_{n-1,n})(\beta_{n,n+1} - ES_{n,n+1})}{E - \alpha_n}, \quad (8)\]
\[\tilde{S}_{n-1,n+1} = 0. \quad (9)\]

Similarly, the substitution of (2) into (3) leads to the rescaled equation
\[(E - \tilde{\alpha}_{n+1})c_{n+1} = (\tilde{\beta}_{n+1,n+1} - ES_{n+1,n+1})c_{n+2} + (\beta_{n+1,n+2} - ES_{n+1,n+2})c_{n+2}. \quad (10)\]

where \(\tilde{\alpha}_{n+1}\) is defined similarly to (7). Taken together, equations (6) and (10) replace (1)-(3) in the set of secular equations, with site \(n\) having been decimated, i.e., deleted from the set, with its effect being incorporated within the renormalized parameters (7)-(9). The process of decimation-renormalization can be repeated, atom by atom, until the original chain or molecule is reduced down to one, or a few, site(s). Looking at the renormalized parameters (7)-(9), it is important to notice that the de facto effect of including overlap is simply to replace \(\beta\) by \(\beta - ES\). Consequently, it is straightforward to extend previous work on benzene transmission so as to incorporate overlap, as in the next section.
4 Benzene Transmission

In considering electron transmission through a benzene molecule, three cases arise, due to the different atomic sites to which the molecular leads can be attached (see Figure 2 of reference [4].) In the para (p)-benzene case, the leads are attached to the (1,4) sites, while in the meta (m)-benzene and ortho (o)-benzene varieties, they are joined to the (1,5) and (1,6) sites, respectively. As shown in detail in [4], the rescaling method is applied in such a way as to successively decimate four of the atoms in the benzene ring, leaving a dimer consisting of the two renormalized sites attached to the leads (which are unaffected by the process). As indicated in the last section, the inclusion of overlap in the rescaling process requires only the replacement of $\beta$ by $\beta - ES$, and subsequently of the reduced energy $X = (E - \alpha)/\beta$ by $X_s = (E - \alpha)/(\beta - ES)$. This substitution is made only in the renormalized parameters, as we are only considering overlap between atoms in the benzene molecule, and not those in the leads. Thus, the zero-overlap results of [4] are readily extended to take overlap into account.

To this end, renormalized parameters for each type of benzene dimer, modified from the results of [4], are as follows.

(a) p-benzene

$$\bar{\alpha}_p \equiv \bar{\alpha}_1 = \bar{\alpha}_4 = \alpha + 2(\beta - ES)X_s(X_s^2 - 1)^{-1},$$

$$\bar{\beta}_p \equiv \bar{\beta}_{14} = 2(\beta - ES)(X_s^2 - 1)^{-1}. \quad (11)$$

(b) m-benzene

$$\bar{\alpha}_m \equiv \bar{\alpha}_1 = \bar{\alpha}_5 = \alpha + (\beta - ES)X_s^{-1}[(X_s^2 - 1)(X_s^2 - 2)^{-1} + 1],$$

$$\bar{\beta}_m \equiv \bar{\beta}_{15} = (\beta - ES)X_s^{-1}(X_s^2 - 1)(X_s^2 - 2)^{-1}. \quad (13)$$

(c) o-benzene

$$\bar{\alpha}_o \equiv \bar{\alpha}_1 = \bar{\alpha}_6 = \alpha + (\beta - ES)X_s^{-1}[1 + (X_sX_s^{-1})^{-1}],$$

$$\bar{\beta}_o \equiv \bar{\beta}_{16} = (\beta - ES)(X_s^2 - 1)(X_s^2 - 2)[(X_s^2 - 1)^2 - X_s^2]^{-1}, \quad (15)$$

with

$$\bar{X}_s = (X_s - X_s^{-1}) - (X_s - X_s^{-1})^{-1}. \quad (17)$$

Also adapted from [4] is the transmission probability, namely,

$$T = \frac{(1 + 2\gamma)^2(4 - X^2)}{(1 - 2Q)^2(4 - X^2) + 4(P - QX)^2}, \quad (18)$$

where

$$P = 2z, \quad Q = z^2 - \gamma - \gamma^2, \quad (19)$$

with

$$z = (\bar{\alpha}_j - \alpha)/2\beta, \quad \gamma = (\bar{\beta}_j - \beta)/2\beta, \quad j = p, m, o, \quad (20)$$

being the reduced dimer-site energies and the intra-dimer coupling, respectively. The index $j$ is chosen so as to represent the desired benzene type, using the appropriate pair of equations from [11] to [16].
5 Results and Discussion

The methodology of the two previous sections can now be implemented to produce the $T(E)$ curves for each of the three benzene types (para-, meta- and ortho-), when overlap is ignored ($S = 0$) and for several non-zero values of $S$. In the following calculations, the parameter values chosen were the atomic-site energy $\alpha = 0$ and the bond energy $\beta = -0.5$, both in the benzene molecules and their leads. As mentioned earlier, overlap $S$ is included only in the benzene molecules, but not the leads, with its value varying from the no-overlap case of $S = 0$ to a maximum of 0.25.

Figure 2 shows the $T(E)$ curves for para-benzene, for the several values of $S$ indicated. The no-overlap case, with $S = 0$, is illustrated in Figure 2(a). The curve is symmetrical in nature, with a pair of resonance maxima near the band edges, and a single local minimum at the band center $E = 0$. Increasing $S$ from 0, even marginally, has the effect of destroying the symmetry of the curve, and diminishing the resonances, although small values of $S$ (see Figure 2(b)) produce otherwise minor changes in $T(E)$. Larger increases in $S$ (see Figure 2(c) and (d)) result in more significant changes, with further decreasing and

![Figure 2: Transmission $T$ versus energy $E$ for para-benzene, with overlap $S = (a) 0$ (green solid curve), (b) 0.1 (red long-dashed), (c) 0.2 (blue dash-dotted), (d) 0.25 (pink short-dashed).](image)
broadening of the lower peak which nonetheless maintains a clear maximum, but more noticeably for the upper peak, which undergoes some narrowing and, eventually, complete suppression. Thus, the asymmetry introduced by overlap shows a greater effect at higher energies, resulting in more favourable conditions for transmission at lower energies.

Turning next to meta-benzene, the case $S = 0$ is shown in Figure 3(a). The curve is symmetrical about the band center, with anti-resonances at $E = 0$ and $E = \pm 0.5$. There are a pair of resonances at $E = \pm 0.71$, and a pair of smaller peaks at $E = \pm 0.37$, bounded by the anti-resonances. This structure, and in particular the anti-resonance at $E = 0$, makes meta-benzene the poorest transmitter of the three benzene types [5]. Taking $S$ to be non-zero (see Figure 3(b)-(d)) again removes the symmetry of the $T(E)$ curve, and all the more so with increasing values of $S$. Interestingly, and unlike the para-benzene case, the resonances are not lowered, but in fact, each is temporarily split into a pair of resonances (Figure 3(b)) before, with increasing $S$, the outer resonance of each pair is gradually lowered until eventually disappearing (Figure 3(c) and (d)). Simultaneously, the lowermost peak broadens somewhat, while the uppermost

![Figure 3: Transmission $T$ versus energy $E$ for meta-benzene, with overlap $S = (a) 0$ (green solid curve), (b) 0.1 (red long-dashed), (c) 0.2 (blue dash-dotted), (d) 0.25 (pink short-dashed).](image)
narrow, due to the anti-resonances at $E = \pm 0.5$ shifting to slightly higher energies (0.66 and -0.4, in Figure 3(d)), while the band edges remain fixed, as does the anti-resonance at $E = 0$. The two smaller peaks flanking $E = 0$ are relatively unchanged, with the lower one increasing and the upper one decreasing marginally, and their widths changed somewhat by the shifting energies of the anti-resonances. As in the previous case, then, the greatest enhancement in $T(E)$ is shown at lower energies, while the least occurs at energies near $E = 0$.

Finally, we consider ortho-benzene, starting from the case $S = 0$, as shown in Figure 4(a). Once again, the $T(E)$ curve is symmetrical, but with no resonances. There is a large central peak with a pair of smaller peaks on each side, separated by anti-resonances at $E = \pm 0.5$ and $E = \pm 0.71$. As in the two previous cases, increasing $S$ from 0 destroys the symmetry (Figure 4(b)-(d)), and indeed, more noticeably than in the other two cases. The change in the central peak is relatively mild, with the maximum increasing somewhat and moving to a slightly lower energy, as $S$ increases. But the real effect is in the side peaks, due partly to the anti-resonances shifting to higher energies, the upper duo more so than the lower pair. Indeed, the uppermost anti-resonance eventually coin-

Figure 4: Transmission $T$ versus energy $E$ for ortho-benzene, with overlap $S =$ (a) 0 (green solid curve), (b) 0.1 (red long-dashed), (c) 0.2 (blue dash-dotted), (d) 0.25 (pink short-dashed).
cides with the upper band edge, so that the uppermost sub-band disappears, all the while as its height is decreasing (Figure 4(c) and (d)). Its neighbouring peak increases substantially in height, while widening as well, to become one the graph’s dominant features. Meanwhile, the lowermost peak broadens and increases immensely to near-resonance status (Figure 4(d)). On the other hand, its neighbouring peak is relatively unaffected, albeit lowered somewhat. Similar to the other two cases, $T(E)$ exhibits its biggest increases at lower energies.

In comparing the effect of overlap in the three cases, it certainly appears that it is greatest for ortho-benzene, and smallest for meta-benzene. For even small non-zero values of $S$, such as 0.05 (not shown in the figures), the symmetry of the $T(E)$ curve is broken, but for such small $S$, the effect is otherwise slight, at least for para- and meta-. The effect increases steadily with increasing $S$. For para- and meta-, the effect is greatest for $S \geq 0.15$, while it is always present for ortho-. In all cases, increasing $S$ has the general effect of shifting $T(E)$ to lower energies.

6 Conclusion

The rescaling technique has been extended, so as to incorporate overlap in the renormalization-decimation equations. Subsequently, the method is applied to our previous work on transmission through benzene molecules, so as to investigate the effect of overlap between the carbon atoms in benzene. The observed effect is quite substantial, with the symmetry of the $T(E)$ curve being broken by even a small degree of overlap, and increasing with $S$. Of the three types, the largest effect occurs for ortho-benzene and the smallest for meta-benzene. These results are indicative that overlap should be included in future studies of benzene transmission.

7 Keywords

Molecular electronics, benzene, overlap, renormalization-decimation technique, semi-empirical calculations

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