Stationary Perturbation Theory with Spatially Well-separated Potentials

Seok Kim and Choonkyu Lee

School of Physics and Center for Theoretical Physics
Seoul National University, Seoul 151-747, Korea

Abstract

We present a new perturbation theory for quantum mechanical energy eigenstates when the potential equals the sum of two localized, but not necessarily weak potentials $V_1(\mathbf{r})$ and $V_2(\mathbf{r})$, with the distance $L$ between the respective centers of the two taken to be quite large. It is assumed that complete eigenfunctions of the local Hamiltonians (i.e., in the presence of $V_1(\mathbf{r})$ or $V_2(\mathbf{r})$ only) are available as inputs to our perturbation theory. If the two local Hamiltonians have degenerate bound-state energy levels, a systematic extension of the molecular orbital theory (or the tight-binding approximation) follows from our formalism. Our approach can be viewed as a systematic adaptation of the multiple scattering theory to the problem of bound states.

∗Electronic address: calaf2@snu.ac.kr
†Electronic address: cklee@phya.snu.ac.kr
I. INTRODUCTION

In one-particle quantum mechanics, consider the energy eigenvalue problem

\[ \hat{H}|\psi\rangle = E|\psi\rangle, \quad (1) \]

when the Hamiltonian of the system has two separate potential contributions, viz.,

\[ \hat{H} = \frac{1}{2m}\hat{p}^2 + \hat{V}_1 + \hat{V}_2. \quad (2) \]

(For simplicity, we will present our discussion within a one-dimensional context). Then one may also consider the related eigenvalue problems

\[ \hat{H}_1|\psi_1\rangle = \varepsilon|\psi_1\rangle, \]
\[ \hat{H}_2|\psi_2\rangle = u|\psi_2\rangle, \quad (3) \]

where

\[ \hat{H}_1 = \frac{1}{2m}\hat{p}^2 + \hat{V}_1, \quad \hat{H}_2 = \frac{1}{2m}\hat{p}^2 + \hat{V}_2. \quad (4) \]

Generally speaking, there will be no simple connection between the eigenvalue problem (1) and those in (3) (other than an inequality-type relation for the ground state energy). But, if \( \hat{V}_1 \) and \( \hat{V}_2 \) correspond to some localized, but not necessarily weak, potentials with the centers at \( x = 0 \) and \( x = L \), respectively and the separation distance \( L \) is relatively large, one might hope that the solutions to the eigenvalue problems in (3) (involving 'local Hamiltonians' \( \hat{H}_1 \) and \( \hat{H}_2 \)) be useful for generating good approximate solutions to the initial problem (1).

Indeed, this view forms the basis of the so-called molecular orbital theory or the tight-binding approximation[1,2], in which one diagonalizes the full Hamiltonian \( \hat{H} \) within the truncated vector space given by a linear combination of atomic orbitals (consisting of a few low-lying eigenstates of the local Hamiltonians). In the context of Born-Oppenheimer approximation where the local potential centers are not really fixed, this kind of energy eigenvalue problem is of particular importance since it can account for an effective binding force between the potential-producing objects.

The tight-binding method or its variants will be useful when given local Hamiltonians allow some deeply-bound orbitals which are separated from other local eigenstates by relatively large energy gap. By its very nature, however, a reliable theoretical error estimate for the scheme (especially when the parameters in the given problem are not quite in the
limiting range for the method) is difficult to make. Also, if one of the local potentials, say, \( \hat{V}_2 \), happens to be strictly repulsive (and so no atomic orbital associated with \( \hat{H}_2 \)) while \( \hat{H}_1 \) allows some bound states, this method is unable to give any useful information on the effect of the potential \( \hat{V}_2 \) on the low-lying eigenstates of the full Hamiltonian (2). There is a related question within the usual tight-binding approximation, that is, on the role of the continuum states in the scheme. Clearly, it is desirable to have a systematic approximation scheme which goes beyond the simplest tight-binding approach. [Recently, Barton et al.[3] discussed the effect of a distant impenetrable wall on quantum mechanical energy levels; but their approach is tuned to the change of the boundary condition, and therefore does not apply to more generic case involving two well-separated potentials.]

In this paper we develop a new stationary perturbation theory which can be used to study the eigenvalue problem with a two-centered Hamiltonian. (For a Hamiltonian with more than two centers a simple extension of our method should be useful.) While there exists a systematic theory dealing with scattering by a multi-centered potential (see Ref.[4] for instance), we are not aware of such development which can be used to study the corresponding bound-state problem in a well-controlled manner. In our approach to the eigenvalue problem (1), it will be assumed that the eigenvalue problems with the local Hamiltonians can be solved explicitly, and so we have at our disposal a complete orthonormal set \( \{|n\rangle\} \) based on eigenstates of \( \hat{H}_1 \) and another complete orthonormal set \( \{\bar{n}\rangle\} \) based on eigenstates of \( \hat{H}_2 \). [The knowledge of the Green’s operators associated with the local Hamiltonians may be assumed instead.] We wish to exploit this over-complete set of basis, which include continuum states, in constructing the bound states of the total Hamiltonian \( \hat{H} \). The result is a perturbation series in which the expansion parameter is a quantity approaching zero as the separation between the local potentials becomes large. [In fact, for strongly localized local potentials, we have an expansion parameter of order \( e^{-\alpha L} \) (\( \alpha \): constant)]. It can be viewed as an expansion in the wave-function stretching factor, that comes with for every \( \hat{V}_2 \) (\( \hat{V}_1 \)) acting on a specific bound state of \( \hat{H}_1 \) (\( \hat{H}_2 \)). This small factor is a direct measure on how much influence one local potential feels from the bound states associated with the other local potential. We also remark that the general philosophy of our formalism is similar to that of the multiple scattering theory[4], but the very nature of the bound-state eigenvalue problems necessitates somewhat different developments.

It should be noted that the standard time-independent perturbation theory is generally
unreliable for our problem. To see that, it suffices to consider the simple situation where one has the bound state energy levels of $\hat{H}_1$ influenced by a strictly positive, well-localized potential $V_2(x)$ at a large distance $L$ (from the center of the potential $V_1(x)$). The strength of $\hat{V}_2$ may not be small, however. If this case can be studied by the usual perturbation theory (that is, by treating $\hat{V}_2$ as a perturbation to the unperturbed Hamiltonian $\hat{H}_1$), the state $|k\rangle$ satisfying $\hat{H}_1|k\rangle = \varepsilon_k|k\rangle$, i.e., that with the unperturbed energy $E^{(0)} = \varepsilon_k ( < 0)$, would acquire the first- and second-order energy shifts

$$E^{(1)} = \langle k|\hat{V}_2|k\rangle,$$

$$E^{(2)} = \sum_{n(\neq k)} \frac{\langle k|\hat{V}_2|n\rangle\langle n|\hat{V}_2|k\rangle}{\varepsilon_k - \varepsilon_n},$$

assuming for simplicity no degeneracy for the unperturbed states. According to (5a), $E^{(1)}$ would be of order $e^{-\frac{2}{\hbar}\sqrt{2m|\varepsilon_k|} L}$. This is nothing but the product of two wave-function stretching factors, as appropriate to the matrix element of $\hat{V}_2$ in a specific bound state of $\hat{H}_1$. The fact is that, according to (5b), $E^{(2)}$ would also be $O(e^{-\frac{2}{\hbar}\sqrt{2m|\varepsilon_k|} L})$ due to the continuum contribution in the intermediate-state sum. This implies that, depending on the strength of $\hat{V}_2$, the second order shift $E^{(2)}$ might be as big as the first-order shift. In an analogous manner, it is not difficult to see that the contributions from the continuum states make the r-th order shift $E^{(r)}$ assume the same order of magnitude as $E^{(1)}$. Hence this is not a valid expansion, and we have to devise a more elaborate scheme to solve our problem.

This paper is organized as follows. In Sec.2, we will concentrate on setting up a reliable perturbation theory with two spatially well-separated potentials in the nondegenerate case. In this discussion we will suppose (mainly to have mathematics under control) that the potentials $V_1$ and $V_2$ are sufficiently well localized; but, we expect that most of our formulas, with suitable adjustments if necessary, remain useful even if these potentials are localized only by some (not too small) powers in the distance from the respective potential centers. Our method is exhibited explicitly for local Hamiltonians involving $\delta-$function potentials. Section 3 is devoted to the extension of this method to the case where the local Hamiltonians $\hat{H}_1$ and $\hat{H}_2$ have (almost-)degenerate energy levels. Here one sees explicitly that, for a reliable perturbation series, a separate treatment in the subspace of degenerate local bound states becomes necessary. The resulting theory is a generalization of the molecular orbital theory that allows one to systematically study higher order corrections, and as such it should have some practical value as well. Section 4 contains concluding remarks. In the Appendix we
present our argument behind the order estimates for various contributions appearing in our perturbation theory (together with some analysis for the example problem).

II. NONDEGENERATE PERTURBATION THEORY

Our goal is to obtain approximate eigenstates of the Hamiltonian \( \hat{H} = \frac{1}{2m} \hat{p}^2 + \hat{V}_1 + \hat{V}_2 \), when complete solutions to the eigenvalue problems with the local Hamiltonians \( \hat{H}_1 (\equiv \frac{1}{2m} \hat{p}^2 + \hat{V}_1) \) and \( \hat{H}_2 (\equiv \frac{1}{2m} \hat{p}^2 + \hat{V}_2) \) are known. In the Hilbert space \( \mathcal{V} \) of the system we have with us two complete orthonormal sets — the set \( \{|n\rangle\} \) based on (discrete and continuous) eigenstates of \( \hat{H}_1 \) and the set \( \{|\bar{n}\rangle\} \) based on eigenstates of \( \hat{H}_2 \). Let \( |k\rangle \) be a given specific nondegenerate bound state of \( \hat{H}_1 \), with eigenvalue \( \varepsilon_k \). We further assume in this section that no eigenstate of \( \hat{H}_2 \) has the eigenvalue equal or very close to \( \varepsilon_k \). Then, if the distance \( L \) between the centers of two local potentials \( V_1(x) \) and \( V_2(x) \) is large enough, we expect that the full Hamiltonian \( \hat{H} \) admit an energy eigenstate \( |\phi_k\rangle \) which should coincide with \( |k\rangle \) in the limit \( L \to \infty \) (i.e., as \( V_2(x) \) is sent away to the very remote). This should be the case irrespectively of the relative magnitude of the two local potentials. Thus, for large \( L \), we may write the solution to the eigenvalue equation

\[
\hat{H} |\phi_k\rangle = E_k |\phi_k\rangle, \quad (\hat{H} = \hat{H}_1 + \hat{V}_2)
\]

as

\[
E_k = \varepsilon_k + \delta E_k, \quad |\phi_k\rangle = |k\rangle + |\delta \phi_k\rangle.
\]

Here the small corrections \( \delta E_k \), \( |\delta \phi_k\rangle \) should satisfy the equation

\[
(\varepsilon_k - \hat{H} + \delta E_k)|\delta \phi_k\rangle = (\hat{V}_2 - \delta E_k)|k\rangle,
\]

which is still exact.

Let us now study the implication of (\ref{eq:8}) in detail. First of all, as in the ordinary stationary perturbation theory, (\ref{eq:8}) does not determine \( |\delta \phi_k\rangle \) uniquely\cite{5}: if \( |\delta \phi_k\rangle \) is a solution of (\ref{eq:8}), so is \( |\delta \phi_k\rangle' = \frac{1}{1+\beta} \left( |\delta \phi_k\rangle - \beta |k\rangle \right) \) for arbitrary constant \( \beta \). As a result, \( \langle k|\delta \phi_k\rangle \) may be chosen as one wishes and the particularly convenient, at least in the ordinary perturbation theory, is the choice

\[
\langle k|\delta \phi_k\rangle = 0,
\]

which is still exact.
i.e., define $|\delta \phi_k\rangle$ in the subspace $\mathcal{V}_k$, the orthogonal complement of $|k\rangle$ in $\mathcal{V}$. With this choice and multiplying both sides of (8) by $\langle k|$ on the left, one obtains

$$\delta E_k = \langle k|\hat{V}_2|k\rangle + \langle k|\hat{V}_2|\delta \phi_k\rangle \quad (= \langle k|\hat{\hat{V}}_2|\phi_k\rangle).$$

(10)

At the same time, one may replace (8) by

$$\hat{Q}_k(\varepsilon_k - \hat{H} + \delta E_k)|\delta \phi_k\rangle = \hat{Q}_k\hat{V}_2|k\rangle,$$

(11)

where $\hat{Q}_k \equiv 1 - |k\rangle\langle k|$. Note that, without the knowledge on $|\delta \phi_k\rangle$, the formula (10) is not informative by itself. To have $|\delta \phi_k\rangle$ determined, one might write (as in the conventional perturbation theory) $|\delta \phi_k\rangle = \sum_{n(\neq k)}|n\rangle\langle n|\delta \phi_k\rangle$ and determine $\langle n|\delta \phi_k\rangle$ with the help of the equations resulting from multiplying (11) by $\langle n|$ on the left. But, as was explained in the introduction, this usual procedure does not lead to a useful perturbation series. (See also discussions further below.)

At this point, recall that, in association with the second local Hamiltonian $\hat{H}_2$, we have another complete set $\{|\bar{n}\rangle\}$ where $\hat{H}_2|\bar{n}\rangle = u_n|\bar{n}\rangle$. We shall utilize them with (8) in a suitable manner. (See (16) below.) Here it is convenient to recast (8) and (11) as

$$\hat{O}|\delta \phi_k\rangle = \hat{V}_2|k\rangle - \delta E_k|k\rangle,$$

(12)

$$\hat{Q}_k\hat{O}|\delta \phi_k\rangle = \hat{Q}_k\hat{V}_2|k\rangle,$$

(13)

introducing the operator

$$\hat{O} \equiv \varepsilon_k - \hat{H} + \delta E_k = \varepsilon_k - \hat{H}_2 - (\hat{\hat{V}}_1 - \delta E_k).$$

(14)

But we are not going to use the condition (9) — it is not convenient for our development. [Note that (11) holds good without assuming this condition]. On $|\delta \phi_k\rangle$ we only demand that it should be small, i.e., suppressed by at least one wave-function stretching factor (accompanying, say, a term like $\hat{V}_2|k\rangle$). If we multiply (12) by $\langle k|$ on the left without imposing (9), we obtain

$$\delta E_k = \frac{\langle k|\hat{V}_2|k\rangle + \langle k|\hat{V}_2|\delta \phi_k\rangle}{1 + \langle k|\delta \phi_k\rangle}.$$  

(15)

From this formula, we may conclude that $\delta E_k$ contains at least two wave-function stretching factors. Now note that, when $\hat{G}_2$ denotes the Green’s operator associated with the second Hamiltonian $\hat{H}_2$

$$\hat{G}_2 \equiv \frac{1}{\varepsilon_k - \hat{H}_2} = \sum_{\bar{n}} \frac{|\bar{n}\rangle\langle \bar{n}|}{\varepsilon_k - u_{\bar{n}}},$$

(16)
the operator $\hat{O}$ satisfies the relation

$$1 = \hat{O}\hat{G}_2 + (\hat{V}_1 - \delta E_k)\hat{G}_2, \tag{17}$$

Hence the right hand side of (13) may be written as $\hat{Q}_k\{\hat{O}\hat{G}_2 + (\hat{V}_1 - \delta E_k)\hat{G}_2\}\hat{V}_2|k\rangle$, and then, by rearranging, we obtain

$$\hat{Q}_k\hat{O}\{|\delta \phi_k\rangle - \hat{G}_2\hat{V}_2|k\rangle\} = \hat{Q}_k\hat{V}_1\hat{G}_2\hat{V}_2|k\rangle - \delta E_k\hat{Q}_k\hat{G}_2\hat{V}_2|k\rangle. \tag{18}$$

This equation is the crucial one for our perturbation scheme.

We wish to solve (18) order by order, with the order in our case determined by the number of the wave-function stretching factors involved. In its left hand side we have the operator $\hat{O}$ acting on a vector yet to be found, $|\psi\rangle \equiv |\delta \phi_k\rangle - \hat{G}_2\hat{V}_2|k\rangle$. Here it is important to note that, if $|\psi\rangle$ does not contain a component proportional to $|k\rangle$, $|\psi\rangle$ and $\hat{O}|\psi\rangle$ would be of the same order due to the assumed nondegenerate nature of $\hat{H}$. As for the component proportional to $|k\rangle$ from $|\psi\rangle$, on the other hand, the situation is not the same: if $\hat{O}$ acts on that piece, the resulting vector will have the order increased by at least one wave-function stretching factor. This follows from

$$\hat{O}|k\rangle = (\varepsilon_k - \hat{H}_1 + \delta E_k - \hat{V}_2)|k\rangle = (\delta E_k - \hat{V}_2)|k\rangle. \tag{19}$$

Based on this observation, the following conclusion should be immediate: in (18), the vector $|\psi\rangle \equiv |\delta \phi_k\rangle - \hat{G}_2\hat{V}_2|k\rangle$ appearing in its left hand side is necessarily of the same order as the expressions in its right hand side, under the proviso that this restriction on the order does not apply to the term proportional to $|k\rangle$. We here make another important observation: the expressions we have in the right hand side of (18) are in fact of higher order than that of $\hat{G}_2\hat{V}_2|k\rangle$. For its justification, see the Appendix. Hence, setting $|\psi\rangle \approx 0$, i.e., $|\delta \phi_k\rangle - \hat{G}_2\hat{V}_2|k\rangle \approx 0$ solves (18) to the leading order. We may thus write

$$|\delta \phi_k^{(1)}\rangle = \hat{G}_2\hat{V}_2|k\rangle \tag{20}$$

and, using this with (13), the following formula for the energy shift results:

$$\delta E_k^{(1)} = \langle k|\hat{V}_2|k\rangle + \langle k|\hat{V}_2\hat{G}_2\hat{V}_2|k\rangle. \tag{21}$$

[Note that $\langle k|\delta \phi_k\rangle$ in the denominator of (13) can be ignored in the leading-order approximation.]
With the expression (16) for $\hat{G}_2$ inserted into (20) and (21), our formulas giving the leading-order correction to the energy eigenstate may be recast as the ones involving the sum over the basis set $\{|\bar{n}\rangle\}$:

$$
|\delta \phi_k\rangle^{(1)} = \sum_{\bar{n}} |\bar{n}\rangle \frac{\langle \bar{n}|\hat{V}_2|k\rangle}{\varepsilon_k - u_{\bar{n}}} ,
$$

$$
\delta E_k^{(1)} = \langle k|\hat{V}_2|k\rangle + \sum_{\bar{n}} \frac{\langle k|\bar{n}\rangle \langle \bar{n}|\hat{V}_2|k\rangle}{\varepsilon_k - u_{\bar{n}}} .
$$

(22)

(23)

Note that, in our procedure, no explicit condition (like that in (9)) has been used to dispense with the ambiguity concerning the $|k\rangle$-component of $|\delta \phi_k\rangle$. Instead, we have decided to choose the simplest available expression for $|\delta \phi_k\rangle$, as suggested by the order-by-order analysis of the relevant equation for our perturbative development. In view of (20), one may well say that our choice in fact corresponds to

$$
\langle k|\delta \phi_k\rangle = \langle k|\hat{G}_2\hat{V}_2|k\rangle + \text{(higher order)}.
$$

(24)

The energy eigenstate we obtain is not properly normalized in general.

Suppose one attacked the above problem with the help of the conventional perturbation theory, regarding $\hat{V}_2$ as a would-be perturbation. Then, instead of (18), one would work with the equation

$$
\hat{Q}_k\hat{O}(|\delta \phi_k\rangle - \hat{G}_1'\hat{V}_2|k\rangle) = \hat{Q}_k\hat{V}_2\hat{G}_1'\hat{V}_2|k\rangle - \delta E_k\hat{Q}_k\hat{G}_1'\hat{V}_2|k\rangle .
$$

(25)

where $\hat{G}_1' = \sum_{n(\neq k)} |n\rangle \langle n|_{\varepsilon_k - \varepsilon_n}$ is the Green’s operator associated with the local Hamiltonian $\hat{H}_1$ (but defined in the orthogonal complement $\mathcal{V}_k$). To obtain (24), one may utilize the equation (33) given below with (13). The lowest-order approximation in the conventional perturbation theory is tantamount to identifying $|\delta \phi_k\rangle$ with the term $\hat{G}_1'\hat{V}_2|k\rangle$. But, in our case, this is not a good approximation (unless the strength of $\hat{V}_2$ itself is very weak), since the first term in the right hand side of (25) can generate a comparable contribution. (See the related discussion in the introduction). Note that we had a different situation with (18) — the expressions in its right hand side were of higher order (i.e., involved more wave-function stretching factors)!

To be convinced of the validity of our leading-order approximations in (22) and (23), let us consider a simple example consisting of a pair of $\delta$-function potentials, i.e.,

$$
V_1(x) = -\gamma_1 \delta(x) , \quad V_2(x) = -\gamma_2 \delta(x - L)
$$

(26)

Then, by straightforward calculations using these eigenfunctions, we find

\[ \phi_0(x) \equiv \langle x | 1 \rangle = \sqrt{\frac{m \gamma_1}{\hbar^2}} e^{-\frac{m \gamma_1}{\hbar^2} x}, \quad \text{(with } \varepsilon_1 = -\frac{m \gamma_1^2}{2 \hbar^2} \text{)} \]  

\[ \xi_0(x) \equiv \langle x | 2 \rangle = \sqrt{\frac{m \gamma_2}{\hbar^2}} e^{-\frac{m \gamma_2}{\hbar^2} (x - L)}, \quad \text{(with } u_2 = -\frac{m \gamma_2^2}{2 \hbar^2} \text{)} \]  

respectively. Now, if the distance between the two local potentials, \( L \), is large (and the value of \( u_2 \) differs from that of \( \varepsilon_1 \) significantly), we expect that the full Hamiltonian \( \hat{H} = \frac{1}{2m} \hat{p}^2 + \hat{V}_1 + \hat{V}_2 \) allow two bound states \( |\phi_1 \rangle \) and \( |\phi_2 \rangle \), which are approximately equal to \( |1 \rangle \) and \( |2 \rangle \), respectively. For this example one can of course find the exact bound state energies by a direct analysis of the corresponding Schrödinger equation. Explicitly, for the state \( |\phi_1 \rangle \), its energy \( E = -\frac{m \gamma_1^2}{2 \hbar^2} \) is determined by the equation

\[ \eta^2 - (\gamma_1 + \gamma_2) \eta + \gamma_1 \gamma_2 (1 - e^{-\frac{4 m \gamma_1}{\hbar^2} \eta}) = 0, \]  

and therefore, for large \( L \), one has

\[ E = -\frac{m \gamma_1^2}{2 \hbar^2} \left\{ 1 + \frac{2 \gamma_2}{\gamma_1} e^{-\frac{2 m \gamma_2}{\hbar^2} L} + \mathcal{O}(e^{-4 \frac{m \gamma_2}{\hbar^2} L}) \right\}. \]  

The above result can also be obtained by using our formula (23). For such check, we need a complete basis \{\( \left\{ \hat{n} \right\} \)\} consisting of the energy eigenstates of \( \hat{H}_2 \): in position space, the desired complete set contains, aside from the bound state \( \xi_0(x) \), two distinct classes of continuum states (both corresponding to energy \( u_q = \frac{h^2 q^2}{2m} \))

\[ \langle x | q(1) \rangle = \frac{1}{\sqrt{\pi}} \cos[q|x - L| + \tan^{-1}\left(\frac{m \gamma_2}{q \hbar^2}\right)], \]  

\[ \langle x | q(2) \rangle = \frac{1}{\sqrt{\pi}} \sin[q|x - L|]. \]  

Then, by straightforward calculations using these eigenfunctions, we find

\[ \langle 1 | \hat{V}_2 | 1 \rangle = -\frac{2 \gamma_2}{\gamma_1} \left( \frac{m \gamma_1^2}{2 \hbar^2} \right) e^{-\frac{m \gamma_1}{\hbar^2} L}, \]  

\[ \frac{\langle 1 | \hat{V}_2 | 2 \rangle \langle 2 | \hat{V}_2 | 1 \rangle}{\varepsilon_1 - u_2} = -\frac{4 (\frac{\gamma_2}{\gamma_1})^2 - 1}{(\frac{\gamma_1}{\gamma_2})^2 - 1} \left( \frac{m \gamma_2^2}{2 \hbar^2} \right) e^{-2 \frac{m \gamma_2}{\hbar^2} L}, \]  

\[ \int_0^\infty dq \frac{\langle 1 | \hat{V}_2 | q(1) \rangle \langle q(1) | \hat{V}_2 | 1 \rangle + \langle 1 | \hat{V}_2 | q(2) \rangle \langle q(2) | \hat{V}_2 | 1 \rangle}{\varepsilon_1 - u_q} = -\frac{2 \gamma_2}{(\frac{\gamma_1}{\gamma_2})^2 + 1} \left( \frac{m \gamma_2^2}{2 \hbar^2} \right) e^{-2 \frac{m \gamma_2}{\hbar^2} L}. \]
By summing these contributions, we thus obtain the result \[ \delta E(1) = -\frac{2\gamma_2}{\gamma_1 - \gamma_2} \left( \frac{m_1^2}{2\hbar^2} \right) e^{-\frac{m_1^2}{\hbar^2}L}, \]
which is in agreement with (30). One may also calculate the first order eigenfunction correction with the help of our formula (22). After some straightforward calculations, we then find
\[ \phi_0(x) + \langle x|\phi_1(1) \rangle = \sqrt{\frac{m\gamma_1}{\hbar^2}} \left\{ e^{-\frac{m_1^2}{\hbar^2}|x|} + \frac{\gamma_2}{\gamma_1 - \gamma_2} e^{-\frac{m_1^2}{\hbar^2}L} e^{-\frac{m_1^2}{\hbar^2}|x-L|} \right\}. \quad (33) \]
This is the correct result, for the exact eigenfunction in the limit \[ e^{-\frac{m_1^2}{\hbar^2}L} \rightarrow 0 \] (with \( \eta = \sqrt{-2\hbar^2E/m} = \gamma_1 + O(e^{-2\frac{m_1^2}{\hbar^2}L}) \) from (23)) can be approximated by
\[ \sqrt{\frac{m\gamma_1}{\hbar^2}} \left\{ e^{-\frac{m_1^2}{\hbar^2}|x|} + \frac{\gamma_2}{\gamma_1 - \gamma_2} e^{-\frac{m_1^2}{\hbar^2}L} e^{-\frac{m_1^2}{\hbar^2}|x-L|} \right\}. \quad (34) \]

Expressions for higher order terms of our perturbation theory can be found also. Here we shall concentrate on identifying the second order terms, since even higher order terms can be found by a rather obvious extension of this procedure. For the purpose, we had better rewrite the contributions in the right hand side of (18) appropriately. As regards the first term, we may here use (instead of (17)) the identity
\[ \hat{Q}_k = \hat{O}G_1' + (\hat{V}_2 - \delta E_k)\hat{G}_1' \quad \left( \hat{G}_1' \equiv \sum_{n(\neq k)} \frac{|n\rangle\langle n|}{\varepsilon_k - \varepsilon_n} \right) \quad (35) \]
to have it rewritten as
\[ \hat{Q}_k \hat{V}_1\hat{G}_2\hat{V}_2|k\rangle = \hat{Q}_k \hat{O}\hat{G}_1'\hat{V}_1\hat{G}_2\hat{V}_2|k\rangle + \hat{Q}_k(\hat{V}_2 - \delta E_k)\hat{G}_1'\hat{V}_1\hat{G}_2\hat{V}_2|k\rangle. \quad (36) \]
On the other hand, with the second term, the relation (17) can be used to write it as
\[ -\delta E_k \hat{Q}_k \hat{G}_2\hat{V}_2|k\rangle = -\delta E_k \hat{Q}_k \hat{O}(\hat{G}_2)\hat{V}_2|k\rangle - \delta E_k \hat{Q}_k(\hat{V}_1 - \delta E_k)(\hat{G}_2)\hat{V}_2|k\rangle. \quad (37) \]
Using these forms with (18) leads, after some rearrangements, to the following equation:
\[ \hat{Q}_k \hat{O} \left\{ |\delta \phi_k \rangle - |\delta \phi_k \rangle^{(1)} - \hat{G}_1'\hat{V}_1\hat{G}_2\hat{V}_2|k\rangle + \delta E_k(\hat{G}_2)\hat{V}_2|k\rangle \right\} = \hat{Q}_k(\hat{V}_2 - \delta E_k)\hat{G}_1'\hat{V}_1\hat{G}_2\hat{V}_2|k\rangle - \delta E_k \hat{Q}_k(\hat{V}_1 - \delta E_k)(\hat{G}_2)\hat{V}_2|k\rangle. \quad (38) \]
In the Appendix the expressions in the right hand side of (38) will be shown to be of higher order than the terms appearing inside the curly bracket in the left hand side of the same equation. Note that, for this behavior, it is crucial to have \( \hat{Q}_k \hat{V}_1\hat{G}_2\hat{V}_2|k\rangle \) rewritten as in (38) and not by the form
\[ \hat{Q}_k \hat{V}_1\hat{G}_2\hat{V}_2|k\rangle = \hat{Q}_k \hat{O}\hat{G}_2\hat{V}_1\hat{G}_2\hat{V}_2|k\rangle + \hat{Q}_k(\hat{V}_1 - \delta E_k)\hat{G}_2\hat{V}_1\hat{G}_2\hat{V}_2|k\rangle. \quad (39) \]
as the use of (17) would result in. [Here the term involving $\hat{V}_1 \hat{G}_2 \hat{V}_1$ is dangerous, when continuum contributions are considered.] On the other hand, as for the term $-\delta E_k \hat{Q}_k \hat{G}_2 \hat{V}_2 |k\rangle$, it is allowed to have (37) replaced by another relation obtained with the use of (35) — but, using (37) (and hence the equation (38)) leads to a simpler perturbation theory practically. Now, based on this order count for the terms appearing on both sides of (38), we are led to conclude that the expression inside the curly bracket may be set to zero in our present approximation. Note that this reasoning is entirely similar to what we used with (18). As a result, it is found that our second order approximation to $|\delta \phi_k\rangle$ can be identified with

$$|\delta \phi_k\rangle^{(2)} = \hat{G}_1' \hat{V}_1 \hat{G}_2 \hat{V}_2 |k\rangle - \delta E_k^{(1)} \hat{G}_2 \hat{G}_2 \hat{V}_2 |k\rangle. \quad (40)$$

By using this expression with (15), one can obtain the corresponding formula for the second-order energy shift also.

For the third or higher order approximation, one may repeat the above procedure. Clearly, the approximation at desired order follows immediately once one has the appropriate generalization of the equation like (18) or (38). As we have explained above, such generalization can always be found by using the identities (17) and (35) in a judicious way with the corresponding equation one order lower. For a useful guideline here, see the Appendix.

III. (ALMOST-) DEGENERATE PERTURBATION THEORY

Our perturbation theory in the previous section was developed under the no degeneracy assumption; that is, for a given unperturbed state $|k\rangle$ (an eigenstate of $\hat{H}_1$ with eigenvalue $\varepsilon_k$), no other eigenstate of $\hat{H}_1$ or $\hat{H}_2$ has the corresponding eigenvalue equal or very close to $\varepsilon_k$. In this section we will dispense with this restrictive assumption. The perturbation theory to be developed below is applicable to the case when (almost-) degeneracy, within the spectrum of $\hat{H}_1$ or between the spectra of the two local Hamiltonians $\hat{H}_1$ and $\hat{H}_2$, is present. This consideration is especially relevant since many physically interesting problems, which were treated traditionally by the molecular orbital theory, do come with such (almost-) degeneracy due to symmetry or by other reasons.

First, we focus on the case when there are two (almost-) degenerate states $|k\rangle$ and $|\bar{k}\rangle$ with $\varepsilon_k \approx u_k$. That is, each local Hamiltonian has a bound state of almost identical energy. [This happens especially if $\hat{H}_2$ is related to $\hat{H}_1$ by a simple spatial translation, i.e., $V_2(x) =$
$V_1(x-L)$. In this case we expect that the exact eigenstate $|\phi_k\rangle$ of the full Hamiltonian $H$ have large overlap with both $|k\rangle$ and $|\bar{k}\rangle$, in accordance with the philosophy of tight-binding approximation. So we may set up our perturbation theory by writing

$$|\phi_k\rangle = |k\rangle + b|\bar{k}\rangle + |\delta \phi_k\rangle$$

(41)

where $|\delta \phi_k\rangle$ is supposed to be small, but the constant $b$ can be a priori $O(1)$. Of course, if $\varepsilon_k$ and $u_k$ were not very close to each other, $b$ would become much smaller than 1.

Inserting the form (41) into the Schrödinger equation (8) then yields

$$\hat{O}|\delta \phi_k\rangle = (\hat{V}_2 - \delta E_k)|k\rangle + b(\hat{V}_1 + u_k - \varepsilon_k - \delta E_k)|\bar{k}\rangle,$$

(42)

where $\delta E_k = E_k - \varepsilon_k$, and $\hat{O}$ is the operator introduced in (14). Here the unknowns are $\delta E_k$, $b$ and $|\delta \phi_k\rangle$, and (42) contains all the conditions required of them.

If we multiply both sides of (42) by $\langle k |$ or $\langle \bar{k} |$ on the left, we obtain two relations which can be used to determine $\delta E_k$ and the constant $b$, given the knowledge on $|\delta \phi_k\rangle$. Explicitly, we may write them as two different expressions for $\delta E_k$, i.e.,

$$\delta E_k = \frac{\alpha + b \Gamma + \langle k | \hat{V}_2 | \delta \phi_k \rangle}{1 + b \Delta + \langle k | \delta \phi_k \rangle},$$

(43)

$$\delta E_k = \frac{b(u_k - \varepsilon_k) + \Gamma + b \beta + (u_k - \varepsilon_k) \langle \bar{k} | \delta \phi_k \rangle + \langle \bar{k} | \hat{V}_1 | \delta \phi_k \rangle}{b + \Delta + \langle k | \delta \phi_k \rangle},$$

(44)

where $\alpha$, $\beta$, $\Gamma$ and $\Delta$ represent the matrix elements

$$\alpha \equiv \langle k | \hat{V}_2 | k \rangle, \quad \beta \equiv \langle \bar{k} | \hat{V}_1 | \bar{k} \rangle,$$

$$\Gamma \equiv \langle k | \hat{V}_2 | \bar{k} \rangle, \quad \Delta \equiv \langle k | \bar{k} \rangle.$$

(45)

[We have used the fact that, when $|k\rangle$ (|\bar{k}\rangle) is a nondegenerate eigenstate of $\hat{H}_1$ ($\hat{H}_2$), it is possible to take $\alpha$, $\beta$, $\Gamma$ and $\Delta$ to be real. To fix the constant $b$ (for given $|\delta \phi_k\rangle$), one can thus solve the quadratic equation obtained by equating the two expressions in the right hand sides of (43) and (44). Then, how can one determine the eigenfunction correction $|\delta \phi_k\rangle$? As in the nondegenerate case considered in Sec.2, an appropriate perturbation theory for $|\delta \phi_k\rangle$ may be set up by considering the restriction imposed by (42) on its components belonging to the space orthogonal to $|k\rangle$ or $|\bar{k}\rangle$. Again, in the corresponding development, we will not impose any specific condition on $\langle k | \delta \phi_k \rangle$ (or, if one wishes, on $\langle k | \delta \phi_k \rangle + b \langle \bar{k} | \delta \phi_k \rangle$); following the order-by-order analysis, it should suffice for us to choose $|\delta \phi_k\rangle$ to be a simplest available expression that is consistent with the equation (42).]
When the separation distance between the local potentials is taken to be large, the leading approximation in our approach corresponds to the standard molecular orbital theory. This can be seen as follows. In (43) and (44), $b$ is order 1 while $|\delta \phi_k\rangle$ is supposed to contain at least one wave-function stretching factor. Also, in the limit we are considering, all four matrix elements in (45) should be quite small; $\alpha$ and $\beta$ contain two wave-function stretching factors, and $\Gamma$ and $\Delta$ one wave-function stretching factor each. In view of the potential $\hat{V}_2$ present in its definition, $\Gamma$ may be estimated to be of order $|u_k|\Delta$. Moreover, from the assumed almost-degeneracy of the two states, it should be natural to assume that

$$|u_k - \varepsilon_k| \ll |u_k|.$$  \hfill{(46)}

With $\Gamma \sim |u_k|\Delta$, this implies $u_k - \varepsilon_k \ll \Gamma/\Delta$ also. Then, in the leading approximation, we may set $|\delta \phi_k(0)\rangle = 0$ (i.e., $|\phi_k\rangle = |k\rangle + b|\bar{k}\rangle$ to this order) and replace the right hand sides of (43) and (44) by $b\Gamma$ and $b(u_k - \varepsilon_k) + \Gamma b$, respectively. From these, we conclude that

$$b(0) = \frac{u_k - \varepsilon_k}{2\Gamma} \pm \sqrt{\left(\frac{u_k - \varepsilon_k}{2\Gamma}\right)^2 + 1}, \quad \delta E_k^{(1)} = \Gamma b(0).$$  \hfill{(47)}

These are what one would expect with the original Hamiltonian replaced by the $2 \times 2$ matrix Hamiltonian (in the space spanned by two atomic orbitals $|k\rangle$ and $|\bar{k}\rangle$)

$$\begin{pmatrix} \varepsilon_k + \alpha & \Gamma \\ \Gamma & u_k + \beta \end{pmatrix},$$  \hfill{(48)}

and with $\alpha$, $\beta$ ignored because they contain two wave-function stretching factors while $\Gamma$ has one. In particular, if $u_k - \varepsilon_k \ll \Gamma$, that is, if two energies are very close, the expressions in (47) tend to the familiar values in the exactly degenerate case, $b(0) \sim \pm 1$ (i.e., $|\phi_k\rangle \sim |k\rangle \pm |\bar{k}\rangle$) and $\delta E_k^{(1)} = \pm \Gamma$. It may also be of interest to look at the case $u_k - \varepsilon_k \gg \Gamma$, that is, when the two energy values are not very close to each other (although they are almost degenerate in the sense of (46)). Then, from the two values given for $b(0)$, only one of them — that with the behavior $b(0) \to 0$ as $\Gamma$ approaches zero — may be chosen since we are seeking for a solution that reduces to $|k\rangle$ in the absence of the potential $V_2$. Hence, with $u_k - \varepsilon_k \gg \Gamma$, we find from (47) the values $b(0) = \frac{r}{\varepsilon_k - u_k}$ and $\delta E_k^{(1)} = \frac{r^2}{\varepsilon_k - u_k}$, which are the results we can infer also on the basis of our formulas (22) and (23) (i.e., the lowest-order results in our nondegenerate formalism).

For higher order corrections, one should look for an iterative solution of (12), as we did the same with (8) in the nondegenerate case. Here, for successive iteration, we will make
use of the relation (instead of (17))

\[ \hat{Q}_k = \hat{O} \hat{G}'_2 + (\hat{V}_1 - \delta E_k) \hat{G}'_2, \]

where \( \hat{Q}_k \equiv 1 - |\bar{k}\rangle \langle k| \), and

\[ \hat{G}'_2 \equiv \hat{Q}_k \hat{G}_2 \hat{Q}_k = \sum_{\bar{n} \neq k} \frac{|\bar{n}\rangle \langle \bar{n}|}{\varepsilon_k - u_{\bar{n}}}. \]

The Green’s operator \( \hat{G}'_1 \), satisfying (33), will be useful as well. But we will here proceed somewhat differently from the nondegenerate case by not utilizing a suitably projected version of (12) in making iteration; for the present (almost-)degenerate case, manipulating directly with (12) is more convenient. Now note that, thanks to (35) and (49), the terms of (42) in making iteration; for the present (almost-)degenerate case, manipulating directly with (12) is more convenient. Now note that, thanks to (35) and (19), the terms \( \hat{V}_2|k\rangle \) and \( \hat{V}_1|\bar{k}\rangle \) in (12) can be rewritten as

\[ \hat{V}_2|k\rangle = \hat{Q}_k \hat{V}_2|k\rangle + |\bar{k}\rangle \langle k| \hat{V}_2|k\rangle \]

\[ = \hat{O} \hat{G}'_2 \hat{V}_2|k\rangle + (\hat{V}_1 - \delta E_k) \hat{G}'_2 \hat{V}_2|k\rangle + \Gamma|\bar{k}\rangle, \]

\[ \hat{V}_1|\bar{k}\rangle = \hat{Q}_k \hat{V}_1|\bar{k}\rangle + |k\rangle \langle k| \hat{V}_1|\bar{k}\rangle \]

\[ = \hat{O} \hat{G}'_1 \hat{V}_1|\bar{k}\rangle + (\hat{V}_2 - \delta E_k) \hat{G}'_1 \hat{V}_1|\bar{k}\rangle + \{\Gamma - (u_{\bar{k}} - \varepsilon_k) \Delta\}|\bar{k}\rangle. \]

Using these in (12) and then collecting all terms involving the operator \( \hat{O} \) explicitly, we obtain the following equation:

\[ \hat{O} \left( |\delta \phi_k\rangle - \hat{G}'_2 \hat{V}_2|k\rangle - b \hat{G}'_1 \hat{V}_1|\bar{k}\rangle \right) = \hat{V}_1 \hat{G}'_2 \hat{V}_2|k\rangle - \delta E_k \hat{G}'_2 \hat{V}_2|k\rangle + b \hat{V}_2 \hat{G}'_1 \hat{V}_1|\bar{k}\rangle - b \delta E_k \hat{G}'_1 \hat{V}_1|\bar{k}\rangle - \{\delta E_k - b \Gamma \left( 1 - \frac{u_{\bar{k}} - \varepsilon_k}{\Gamma/\Delta} \right) \}|\bar{k}\rangle - \{b \delta E_k - \Gamma\}|\bar{k}\rangle. \]

Based on (53), we will now show that the leading approximation for \( |\delta \phi_k\rangle \) can be taken as

\[ |\delta \phi_k\rangle^{(1)} = \hat{G}'_2 \hat{V}_2|k\rangle + b \hat{G}'_1 \hat{V}_1|\bar{k}\rangle. \]

First note that, as in the nondegenerate case, the first four terms in the right hand side of (53) can be shown to be of higher order than the expression \( \hat{G}'_2 \hat{V}_2|k\rangle + b \hat{G}'_1 \hat{V}_1|\bar{k}\rangle \). On the other hand, the last two terms in the right hand side of (53) are explicitly proportional to \( |k\rangle \) or \( |\bar{k}\rangle \); they are present because we are not working with a projected equation. Still, we observe that these terms are also smaller than the expression \( \hat{G}'_2 \hat{V}_2|k\rangle + b \hat{G}'_1 \hat{V}_1|k\rangle \), if the lowest order values for \( \delta E_k \) and \( b \) in (17) are used. [Here remember that \( \frac{u_{\bar{k}} - \varepsilon_k}{\Gamma/\Delta} \ll 1 \).] Then, based on these and our earlier observation as regards the effect of the operator \( \hat{O} \) (in that case with (18)), the identification (54) can be made.
The expression (54), with \( b \) replaced by \( b^{(0)} \), may in turn be used in (13) and (14) to find the second order energy shift \( \delta E_k^{(2)} \) and the value \( b^{(1)} \). The results, to the appropriate order in the wave-function stretching factor (but without making an expansion with respect to another small factor \( \frac{|u_k - \varepsilon_k|}{\gamma} \)), read

\[
b^{(1)} = \left\{ \frac{\beta - \alpha}{2\Gamma} + \frac{\langle \hat{k}|\hat{V}_1\hat{G}'_1\hat{V}_1|\hat{k} \rangle - \langle k|\hat{V}_2\hat{G}'_2\hat{V}_2|k \rangle}{2\Gamma} \right\} \left\{ 1 \pm \frac{u_k - \varepsilon_k}{2\Gamma} \right\}, \tag{55}
\]

\[
\delta E_k^{(2)} = \Gamma b^{(1)} + \alpha + \langle k|\hat{V}_2\hat{G}'_2\hat{V}_2|k \rangle - \Gamma \Delta(b^{(0)})^2. \tag{56}
\]

Especially, with \( u_k = \varepsilon_k \), i.e., in exactly degenerate case, (56) reduces to

\[
\delta E_k^{(2)} = \frac{\langle k|\hat{V}_2|k \rangle + \langle k|\hat{V}_2\hat{G}'_2\hat{V}_2|k \rangle}{2} + \frac{\langle \hat{k}|\hat{V}_1|\hat{k} \rangle + \langle \hat{k}|\hat{V}_1\hat{G}'_1\hat{V}_1|\hat{k} \rangle}{2} - \langle k|\hat{k} \rangle \langle k|\hat{V}_2|\hat{k} \rangle, \tag{57}
\]

as the definitions for \( \alpha, \beta, \Gamma \) and \( \Delta \) in (15) are used. According to this formula, the second order energy shifts for the two split states become identical. An explicit check for the validity of (57) may be made for our \( \delta \)-function example (see (26)) with \( \gamma_1 = \gamma_2 \equiv \gamma \). According to the direct calculation based on (29), we have \( \delta E_k^{(2)} = -\frac{m^2}{2h^2} \left( 2\frac{m\gamma L}{k} + 1 \right) e^{-2\frac{m\gamma L}{k}} \). We have verified that this very result is reproduced when various terms in (57) are explicitly evaluated. Also, as in the nondegenerate case, a further rearrangement of (53) may be considered to obtain the expressions for the next order contributions. But, because of the complications involved and because their usefulness is rather limited, we will not consider such further higher order terms.

It is possible to generalize the above discussion to the case when there are more than two degenerate states, that is, \( N_1 \) eigenstates \( \{|k_\mu \rangle : \mu = 1, \ldots, N_1 \} \) of \( \hat{H}_1 \) with the given energy \( \varepsilon_k \) and \( N_2 \) eigenstates \( \{|\bar{k}_\bar{\mu} \rangle : \bar{\mu} = 1, \ldots, N_2 \} \) of \( \hat{H}_2 \), with the same energy \( u_{\bar{k}} = \varepsilon_k \). Here we will concentrate on exactly degenerate case, not to make the problem too complicated. Now, for the exact eigenstates of the total Hamiltonian, we may write

\[
|\phi \rangle = \sum_\mu a_\mu |k_\mu \rangle + \sum_{\bar{\mu}} b_{\bar{\mu}} |\bar{k}_{\bar{\mu}} \rangle + |\delta \phi \rangle, \tag{58}
\]

where \( a_\mu \) and \( b_{\bar{\mu}} \) can be \( \mathcal{O}(1) \), but \( |\delta \phi \rangle \) is small. Inserting this form into the Schrödinger equation (1), we obtain an equation similar to (12),

\[
\hat{O}|\delta \phi \rangle = \sum_\mu a_\mu (\hat{V}_2 - \delta E_k)|k_\mu \rangle + \sum_{\bar{\mu}} b_{\bar{\mu}} (\hat{V}_1 - \delta E_k)|\bar{k}_{\bar{\mu}} \rangle. \tag{59}
\]
Then, from multiplying both sides of this equation by \( \langle k_\mu \rangle \) and \( \langle \bar{k}_\bar{\mu} \rangle \) from the left, we obtain the following conditions which may be used to determine \( \delta E \), \( a_\mu \) and \( b_\bar{\mu} \):

\[
\delta E(a_\mu + \sum_\nu \Delta_{\mu\nu} b_\nu + \langle k_\mu | \delta \phi \rangle) = \sum_\nu \Gamma_{\mu\nu} b_\nu + \sum_\nu \alpha_{\mu\nu} a_\nu + \langle k_\mu | \bar{V}_2 | \delta \phi \rangle, \\
\delta E(b_\bar{\mu} + \sum_\nu \Delta_{\bar{\mu}\bar{\nu}} a_\nu + \langle \bar{k}_\bar{\mu} | \delta \phi \rangle) = \sum_\nu \Gamma_{\bar{\mu}\bar{\nu}} a_\nu + \sum_\nu \beta_{\bar{\mu}\bar{\nu}} b_\nu + \langle \bar{k}_\bar{\mu} | \bar{V}_1 | \delta \phi \rangle,
\]

where we have defined

\[
\alpha_{\mu\nu} \equiv \langle k_\mu | \bar{V}_2 | k_\nu \rangle, \quad \beta_{\bar{\mu}\bar{\nu}} \equiv \langle \bar{k}_\bar{\mu} | \bar{V}_1 | \bar{k}_\bar{\nu} \rangle, \\
\Gamma_{\mu\nu} \equiv \langle k_\mu | \bar{V}_1 | \bar{k}_\bar{\nu} \rangle = \langle k_\mu | \bar{V}_2 | \bar{k}_\bar{\nu} \rangle, \quad \Delta_{\mu\nu} \equiv \langle k_\mu | k_\nu \rangle,
\]

and \( \dagger \) denotes the hermitian conjugate. [Note that \( \Gamma \) and \( \Delta \) are \( N_1 \times N_2 \) matrices — not square matrices in general.]

To determine the lowest order values \( \delta E^{(1)} \), \( a_\mu^{(0)} \) and \( b_\bar{\mu}^{(0)} \), we note that (60) and (61), as only leading order terms are kept, imply the following equations:

\[
\delta E^{(1)} a_\mu^{(0)} = \sum_\nu \Gamma_{\mu\nu} b_\nu^{(0)}, \quad (\mu = 1, \cdots, N_1) \\
\delta E^{(1)} b_\bar{\mu}^{(0)} = \sum_\nu \Gamma_{\bar{\mu}\bar{\nu}} a_\nu^{(0)}, \quad (\bar{\mu} = 1, \cdots, N_2).
\]

These can be regarded as a single eigenvector equation for an \((N_1+N_2)\)-vector \((a^{(0)}, b^{(0)})\),

\[
\begin{pmatrix}
0 & \Gamma \\
\Gamma^\dagger & 0
\end{pmatrix}
\begin{pmatrix}
a^{(0)} \\
b^{(0)}
\end{pmatrix} = \delta E^{(1)}
\begin{pmatrix}
a^{(0)} \\
b^{(0)}
\end{pmatrix}.
\]

This is equivalent to the molecular orbital theory approximation [1,2] in which the full Hilbert space is truncated to the finite-dimensinal space spanned by \( N_1+N_2 \) atomic orbitals, i.e., \( \{ |k_\mu \rangle \} \) and \( \{ |\bar{k}_{\bar{\mu}} \rangle \} \). Assuming \( N_1 \geq N_2 \), the \( N_1+N_2 \) eigenvectors and corresponding eigenvalues may schematically be expressed by the forms

\[
(a_{I\mu}^{(0)}, b_{I\bar{\mu}}^{(0)}) = (u_{I\mu}, \pm v_{I\mu}), \quad \delta E_{I}^{(1)} = \pm \lambda_I, \quad \text{for } I = 1, 2, \cdots N_2 \\
(a_{J\bar{\mu}}^{(0)}, b_{J\mu}^{(0)}) = (U_{J\mu}, 0), \quad \delta E_{J}^{(1)} = 0, \quad \text{for } J = 2N_2 + 1, \cdots N_1 + N_2.
\]

The first \( 2N_2 \) eigenvectors are given by \( N_2 \) pairs of states, i.e., \( \{ \sum_\mu u_{I\mu} |k_\mu \rangle \pm \sum_\mu v_{I\bar{\mu}} |\bar{k}_{\bar{\mu}} \rangle ; I = 1, \cdots, N_2 \} \), with respective energy splits \( \pm \lambda_I \). [Here, from studying (64), it can be shown that \( \sum_\mu u_{I\mu}^* u_{I\mu} = \sum_\mu v_{I\bar{\mu}}^* v_{I\bar{\mu}} \) for each \( I = 1, 2, \cdots, N_2 \), and so all \( u_{I\mu} \), \( v_{I\mu} \) may be taken to be unit vectors.] If the eigenvalue set \( \{ \pm \lambda^I \} \) contains zero or the same value more than once, the degeneracy is not completely lifted and one may have to perform higher order analysis for
the effect (and associated true energy eigenvectors). There is no first-order energy shift for
the remaining \( N_1 - N_2 \) eigenstates, represented by \( \{ \sum \mu U_{\mu \nu} |k_{\mu}\rangle \, : \, J = 2N_2 + 1, \ldots, N_1 + N_2 \} \).

Hence, with \( N_1 > N_2 \), there always remains some energy degeneracy which is not lifted by
the lowest order consideration alone.

To develop the corresponding higher-order perturbation theory, one should now take the
expressions

\[
\hat{G}_1' \equiv \sum_{n(\neq k_{\mu})} \frac{|n\rangle \langle n|}{\varepsilon_k - \varepsilon_n}, \quad \hat{G}_2' \equiv \sum_{\bar{n}(\neq k_{\mu})} \frac{|\bar{n}\rangle \langle \bar{n}|}{\varepsilon_k - \bar{n}_{\bar{n}}}
\]

as relevant Green’s functions and proceed in more or less the same manner as in our earlier
consideration. Especially, with \( N_1 = N_2 = N \), we then find the results (as direct generaliza-
tions of (64) and (65))

\[
|\delta \phi_I^{(1)}\rangle = \sum_{\mu, \nu} u_{I\mu} \hat{G}_2' \hat{V}_2 |k_{\mu}\rangle \pm \sum_{\mu} v_{I\mu} \hat{G}_1' \hat{V}_1 |k_{\mu}\rangle,
\]

\[
\delta E_I^{(2)} = \frac{1}{2} \sum_{\mu, \nu} u_{I\mu}^* \left\{ \alpha_{\mu \nu} + \langle k_{\mu}| \hat{V}_2 \hat{G}_2' \hat{V}_2 |k_{\nu}\rangle \right\} u_{I\nu} + \frac{1}{2} \sum_{\mu, \bar{\nu}} v_{I\mu}^* \left\{ \beta_{\mu \bar{\nu}} + \langle k_{\mu}| \hat{V}_1 \hat{G}_1' \hat{V}_1 |k_{\bar{\nu}}\rangle \right\} v_{I\bar{\nu}} - \frac{\lambda_I}{2} \sum_{\mu, \nu} \left\{ u_{I\mu}^* \Delta_{\mu \nu} v_{I\nu} + v_{I\nu}^* \Delta_{\nu \mu}^* u_{I\mu} \right\},
\]

where we have normalized \( u_I \) and \( v_I \) to be unit vectors.

With \( N_1 > N_2 \), we need to consider also the higher order terms to determine the above
\( N_1 - N_2 \) eigenvectors \( \{ \sum \mu U_{I\mu} |k_{\mu}\rangle \, : \, J = 2N_2 + 1, \ldots, N_1 + N_2 \} \) unambiguously and the possible
energy splitting between them. To that end, one has to study the second order contributions
from (60). Let us here assume for simplicity that the \( (N_1 - N_2) \)-dimensional space spanned
by the states \( \sum_{\mu} U_{I\mu} |k_{\mu}\rangle \) represent the entire subspace with \( \delta E^{(1)} = 0 \) in the space of atomic
orbitals. Then observe that, in view of the second relation in (63), this \( (N_1 - N_2) \)-dimensional space with \( \delta E^{(1)} = 0 \) can be identified with the kernel of the matrix \( \Gamma^\dagger \). One now finds from (61) that the (yet unknown) coefficients \( U_{J\mu} \) should be associated with the solutions of

\[
\delta E_J^{(2)} U_{J\mu} = \sum_{\nu} \alpha_{\mu \nu} U_{J\nu} + \sum_{\bar{\nu}} \Gamma_{\mu \bar{\nu}} b^{(1)}_{J\bar{\nu}} + \langle k_{\mu}| \hat{V}_2 |\delta \phi_J^{(1)}\rangle,
\]

for \( |\delta \phi_J^{(1)}\rangle \) expressed in terms of \( U_{J\mu} \) through \( |\delta \phi_J^{(1)}\rangle = \sum_{\mu} U_{J\mu} \hat{G}_2' \hat{V}_2 |k_{\mu}\rangle \) (see (67)). Actually,
in (63), it can be shown (using the property \( \sum_{\nu} \Gamma_{\mu \nu}^\dagger U_{J\nu} = 0 \)) that the term \( \sum_{\bar{\nu}} \Gamma_{\mu \bar{\nu}} b^{(1)}_{J\bar{\nu}} \) is
irrelevant to this order, and therefore (69) is really an eigenvector equation for the vectors
\( U_{J\mu} \):

\[
\delta E_J^{(2)} U_{J\mu} = \sum_{\nu} \left( \langle k_{\mu}| \hat{V}_2 |k_{\nu}\rangle + \langle k_{\mu}| \hat{V}_2 \hat{G}_2' \hat{V}_2 |k_{\nu}\rangle \right) U_{J\nu}.
\]
This equation may be used to determine the coefficients $U_{J\mu}$ and the energy shifts $\delta E_J^{(2)}$. As one can see from this consideration, our perturbative formalism can deal with essentially all situations regarding the bound-state problem with well-separated potentials.

**IV. CONCLUDING REMARKS**

In this paper we have presented a systematic perturbation theory for energy eigenstates when the potential of the system consists of two spatially well-separated pieces, under the assumption that complete energy eigenstates of the two local Hamiltonians are available for our use. Our perturbative development, an expansion in the number of wave-function stretching factors, is reminiscent of the multiple scattering series. Depending on whether the local Hamiltonians have (almost-)degenerate energy levels or not, different perturbation theories must be used. Especially, when the local Hamiltonians have degenerate energy levels, one obtains from our theory systematic higher-order correction terms beyond the predictions of the molecular orbital theory. The reasonably simple formulas we found for the leading correction terms, that is, (20) and (21) in the nondegenerate case and (54)-(57) (or (67)-(70)) in the degenerate case, may have some immediate practical applications.

Extension to the case with more than two spatially localized potentials (in fact even to the case of a lattice of potentials) should be straightforward. Also, if the degenerate atomic orbitals are present in association with certain symmetry in the system, one may utilize so-called symmetry-adapted linear combinations of atomic orbitals[1,2] to simplify the perturbation theory. But we have not made any systematic attempt in this direction. We also remark that if the local potentials happen to be not sufficiently well-localized (i.e., individual potentials have some long-range tails), certain rearrangements may become necessary with our perturbation series. This case deserves further study. One can also contemplate on a simple field-theoretic application: perturbation theory similar to the one given in this paper may be used to study the fermionic bound states associated with a soliton-antisoliton pair[4].

**ACKNOWLEDGEMENTS**

This work was supported in part by the BK21 project of the Ministry of Education, Korea, and the Korea Research Foundation Grant 2001-015-DP0085.
APPENDIX

In this appendix we will first present the argument that shows why the terms in the right hand sides of (18) and (38) are expected to be of higher order than those terms in the left hand sides of the respective equations. We will then make estimates, by general argument and by considering explicitly the case of $\delta$-function potentials, on how small the suppressed continuum contributions might be.

Let us start with our equation (18), used for the leading order approximation, and (25) for comparison’s sake. The two candidates one wishes to identify as the leading-order expression of $|\delta\phi_k\rangle$, i.e., $\hat{G}_2\hat{V}_2|k\rangle$ according to (18) and $\hat{G}_1'\hat{V}_2|k\rangle$ from (25), contain one wave-function stretching factor coming from the overlap of $\hat{V}_2$ and $|k\rangle$. Since $\delta E_k$ carries at least two wave-function stretching factors, the last terms in the right hand sides of (18) and (25) can safely be ignored in lowest order consideration. Here, the dangerous terms are the ones without $\delta E_k$, i.e., $\hat{V}_1\hat{G}_2\hat{V}_2|k\rangle$ in (18) and $\hat{V}_2\hat{G}_1'\hat{V}_2|k\rangle$ in (25). Both have clearly one wave-function stretching factor from $\hat{V}_2|k\rangle$, and one might expect that an additional suppression might result from the combination $\hat{V}_1\hat{G}_2\hat{V}_2$ or $\hat{V}_2\hat{G}_1'\hat{V}_2$. The Green’s operators $\hat{G}_1'$ and $\hat{G}_2$ come with the sum over appropriate energy eigenstates (of the local Hamiltonians $\hat{H}_1$, $\hat{H}_2$), which include the continuum. As for the bound state contributions of one local Hamiltonian to the Green’s operator, there should be such additional suppression (due to small overlap) if they get combined with the potential of the other local Hamiltonian. But, for the contribution to the Green’s operator from continuum states which are not localized at all, one might not expect such suppression factor to show up, for these continuum states would apparently have more or less equal overlap regardless of the ‘location’ of the other potential. But this ignores the fact that one should really consider the net effect of entire continuum states. As will be discussed below, we get a very different picture after integrating over the continuum.

Representing the continuous eigenstates of $\hat{H}_2$ by $|\bar{q}\rangle$, we may express the continuum contribution of $\hat{V}_1\hat{G}_2\hat{V}_2$ as

$$\int d\bar{q} \frac{\hat{V}_1|\bar{q}\rangle\langle\bar{q}|\hat{V}_2}{\varepsilon_k - u_{\bar{q}}}.$$  (71)

Here, for well-localized potentials $V_1$ and $V_2$, the vectors $\hat{V}_1|\bar{q}\rangle = \int dx|x\rangle V_1(x)|\bar{q}\rangle$ and $\langle\bar{q}|\hat{V}_2 = \int dy\langle\bar{q}|y\rangle V_2(y)|y\rangle$ will receive nonnegligible contributions mainly from the regions around the respective potential centers, i.e., $x = 0$ and $y = L$. Furthermore, outside the range of the potential $V_2$, the function $\langle x|\bar{q}\rangle$ may well be approximated by a plane wave. This implies
that $\hat{V}_1|q\rangle\langle q|\hat{V}_2$ comes with a phase factor $\langle x(\approx 0)|\hat{V}_1|q\rangle\langle q|\hat{V}_2|y(\approx L)\rangle \sim e^{i\bar{q}L}$, which causes a destructive interference if the separation $L$ is sufficiently large. Hence the term in (71) comes with desired additional suppression. On the other hand, an analogous consideration with the continuum contribution of $\hat{V}_2\hat{G}_1'\hat{V}_2$ does not lead to such a fast oscillating factor and so no suppression after summing over all corresponding continuum states. This explains why, for our leading order analysis, we can utilize (18), but not (25).

By same reasoning as above, we expect that the continuum contributions for, say, $\langle k|\hat{G}_2\hat{V}_2$ or $\hat{V}_2(\hat{G}_1')^n\hat{V}_1$ (with $n \geq 2$) be also suppressed. Suppression in the former case follows since $\hat{G}_2$ appears between the bound state $|k\rangle$, which is localized around the center of $V_1$, and the potential $V_2$ (localized around $x = L$). As for the latter, the continuum contributions from $(\hat{G}_1')^n$ give rise to a rapidly oscillating phase if sandwiched between $\hat{V}_1$ and $\hat{V}_2$. This suggests also a useful guideline in our consideration of higher order perturbation terms: to have the continuum contributions from $\hat{G}_1'$ and $\hat{G}_2$ suppressed as much as possible, we had better iterate the relevant equation so that such Green’s operator may take its place between $\hat{V}_1$ (or $|k\rangle$) and $\hat{V}_2$. In fact, we followed this guideline to obtain the expression for $|\delta\phi\rangle^{(2)}$, i.e., when we proceeded from (18) to (38). Of course, to confirm that (38) leads to the identification (10) for $|\delta\phi\rangle^{(2)}$, we need to pay more careful attention to the order of various terms appearing in (38), and especially demonstrate the relative higher-order nature for the expression on its right hand side. For this, see below.

First, with (38), look at the terms appearing inside the curly brackets on its left hand side. Based on (20), we know that $|\delta\phi_{k}\rangle^{(1)}$ is of order $e^{-\frac{1}{\hbar}\sqrt{2m|\varepsilon_k|}}L$; the suppression factor here originates from the exponential tail of the bound state $|k\rangle$. With the next term $\hat{G}_1'\hat{V}_1\hat{G}_2\hat{V}_2|k\rangle$, we note that (aside from $\hat{V}_2|k\rangle$, itself of order $e^{-\frac{1}{\hbar}\sqrt{2m|\varepsilon_k|}}L$) there is another small factor, say $\kappa_2$, coming from $\hat{V}_1\hat{G}_2\hat{V}_2$. That is, this term is of order $\kappa_2e^{-\frac{1}{\hbar}\sqrt{2m|\varepsilon_k|}}L$. The last term, $\delta E_k(\hat{G}_2)^2\hat{V}_2|k\rangle$, is of order $\{e^{-\frac{1}{\hbar}\sqrt{2m|\varepsilon_k|}}L\}^3$. Between $\hat{G}_1'\hat{V}_1\hat{G}_2\hat{V}_2|k\rangle$ and $\delta E_k(\hat{G}_2)^2\hat{V}_2|k\rangle$ we can not say generally which one is larger, because the magnitude of $\kappa_2$ depends on the specific problem under study. Therefore, it is appropriate to include both terms in our second order approximation, under the understanding that only one term may well be dominant over the other in a given specific problem. Similar analysis can also be made for various terms in the right hand side of (38). If we denote the small factors emerging from $\hat{V}_2\hat{G}_1'\hat{V}_1$ and $\hat{V}_1(\hat{G}_2)^2\hat{V}_2$
by $\kappa_1$ and $\kappa'_2$, respectively, we here find

$$\hat{V}_2\hat{G}_1^\dagger\hat{V}_1G_2\hat{V}_2|k\rangle \sim \kappa_1\kappa_2e^{-\frac{i}{\hbar}\sqrt{2m|\varepsilon_k|L}},$$

$$\delta E_k\hat{V}_1(G_2)^2\hat{V}_2|k\rangle \sim \kappa'_2(e^{-\frac{i}{\hbar}\sqrt{2m|\varepsilon_k|L}})^3,$$

This shows that the terms in the right hand side of (38) are relatively of higher order, as compared with those terms appearing inside the curly brackets on its left hand side. [Note that this is true without any extra assumption about the relative ratios between $\kappa_1$, $\kappa_2$ and $\kappa'_2$]. Hence our formula for the second order correction $|\delta\phi_k^{(2)}\rangle$ in (40) follows.

In the above discussion, various small factors like $\kappa_1$, $\kappa_2$ have been introduced. How small are the continuum contributions associated with these factors? Consider $\hat{V}_2\hat{G}_1^\dagger\hat{V}_1$, with the related continuum contribution given by

$$\int dx dy \int dq V_2(x)\psi_q(x+L)\psi_q^*(y) -|\varepsilon_k| - \frac{\hbar^2 q^2}{2m} V_1(y),$$

where $\psi_q(x) \equiv \langle x|q \rangle$, a continuous eigenstate of $\hat{H}_1$. Here, for well-localized local potentials, the integral will get most of its contribution from the neighborhood of $x, y \sim 0$. For fixed $x$ in the neighborhood, we may then extract the leading $L$-dependence from $\psi_q(x+L)$ as

$$\psi_q(x) \approx A(q)e^{i\Delta(k)}e^{iq(L+x)},$$

where $A(q)$, $\Delta(k)$ represent the amplitude and phase shift, respectively. With the form (74) used in (73), and after some careful study of the $q$-dependence including that from $\psi_q^*(y)$, we notice that the given amplitude takes the form

$$\int_{-\infty}^{\infty} dq \, f(q, x, y)e^{ikL},$$

where $f$ corresponds to some regular function in $q$. For $L$ very large, the order of magnitude for this integral can be deduced with the help of the Riemann-Lesbegue lemma[6]: if the $n$-th derivative of $f(q)$ satisfies the so-called Dirichlet condition, then

$$\int_{-\infty}^{\infty} f(q)e^{ikL} \sim O\left(\frac{1}{L^{n+1}}\right).$$

Thus, for regular $f$, the integral should be smaller than any power of $\frac{1}{L}$. This strongly suggests that the typical large-$L$ behavior of the integral (74) is that of an exponential suppression (i.e., vanishes like $e^{-\alpha L}$, $\alpha$ being some positive constant). Remaining integrations
with respect to the variables $x$ and $y$ will not change this order estimate in any significant way, and so $\kappa_1$ is exponentially suppressed for large $L$. By analogous arguments one may demonstrate that $\kappa_2$ and $\kappa'_2$, for large $L$, are also exponentially small.

It is possible to give more precise large-$L$ dependences for the factors $\kappa_1$, $\kappa_2$ and $\kappa'_2$ if a concrete problem is considered. For instance, we can compute these factors explicitly when the problem is that of a pair of $\delta$-function potentials as given in (26). Then, using the corresponding continuum wave-functions (see (31)), we obtain

$$\kappa_1 = -\frac{2m\gamma_1\gamma_2}{\hbar^2} \int_0^{\infty} dq \frac{\langle x = L | q^{(1)} \rangle \langle q^{(1)} | y = 0 \rangle}{q^2 + \left( \frac{m\gamma_1}{\hbar^2} \right)^2} = \gamma_2 \left( \frac{m\gamma_1 L}{\hbar^2} - \frac{1}{2} \right) e^{-\frac{m\gamma_1 L}{\hbar^2}},$$

$$\kappa_2 = \frac{\gamma_1\gamma_2}{\gamma_1 - \gamma_2} \left\{ \frac{2\gamma_2}{\gamma_1 + \gamma_2} e^{-\frac{m\gamma_2 L}{\hbar^2}} - e^{-\frac{m\gamma_1 L}{\hbar^2}} \right\},$$

$$\kappa'_2 = \frac{4\hbar^2 \gamma_1\gamma_2}{m} \left\{ -\frac{\gamma_2}{(\gamma_1^2 - \gamma_2^2)^2} e^{-\frac{m\gamma_2 L}{\hbar^2}} + \frac{1}{\gamma_2^2(\gamma_1 - \gamma_2)} \left( \frac{m\gamma_1 L}{\hbar^2} + \frac{\gamma_1}{\gamma_1 - \gamma_2} \right) e^{-\frac{m\gamma_1 L}{\hbar^2}} \right\}.$$ (77)

As anticipated, we see the exponential dependences on $L$ for these factors. We also observe from the results (77)-(79) that, depending on the relative magnitudes of $\gamma_1$ and $\gamma_2$, it may be just one term that dominates the respective expression. Furthermore, as the result (78) for $\kappa_2$ is used in our formula (40), we notice that the second term (proportional to $\delta E^{(1)}_{k}$) is negligible compared to the first. Hence, for this example, we are allowed to write

$$|\delta \phi_k^{(2)} \rangle = \hat{G}'_1 \hat{V}_1 \hat{G}_2 \hat{V}_2 |k \rangle = \kappa_2 \sqrt{\frac{m\gamma_1}{\hbar^2}} e^{-\frac{m\gamma_1 L}{\hbar^2}} \hat{G}'_1 |x = 0 \rangle.$$ (80)

[1] P.W. Adkins and R.S. Friedman, “Molecular Quantum Mechanics”, 3rd ed. (Oxford University Press, 1997); J.D. Roberts, “Notes on Molecular Orbital Calculations” (W.A. Benjamin, Inc., New York, 1962).

[2] M. Tinkham, “Group Theory and Quantum Mechanics” (McGraw-Hill, 1964).

[3] G. Barton, A.J. Bray and A.J. McKane, Am. J. Phys. 58 : 751, 1990.

[4] M. Goldberger and K.M. Watson, Collision Theory, John Wiley, 1964.

[5] See, for instance, E. Merzbacher, “Quantum Mechanics”, 3rd ed. (John Wiley & Sons, 1998); J.J. Sakurai, “Modern Quantum Mechanics”, revised ed. (Addison Wesley, 1994).

[6] See, for instance, E.T. Whittaker and G.N. Watson, A course of Modern Analysis, 4th ed. (Cambridge University Press, 1996).

[7] B. Altschul, hep-th/0111042.