Chemistry of vibronic coupling. Part 1: How to maximize vibronic coupling constants in a diabatic harmonic potential model?

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Abstract

Using a simple diabatic model of two equivalent energy minima with crossing harmonic potential energy surfaces, we analyze the vibronic coupling constant \( \lambda_{eg} \) (expressed in energy units) is a product of \( h_{eg} \) (expressed in force units) and \( \langle u_i|Q|v_i \rangle \) (expressed in distance units) where \( h_{eg} \) is the dynamic off-diagonal vibronic coupling constant, \( u_i \) and \( v_i \) are vibrational wave functions for normal mode \( i \) in the \( g \) and \( e \) state respectively, and \( Q_i \) is normal coordinate of \( i \)th mode. We study the way \( \lambda_{eg} \) depends on three parameters: the force constant \( (k) \), the reduced oscillator mass \( (m) \) and the displacement between two minima along the normal coordinate of the coupling mode \( Q_i \). For each \( k \) there is only one \( \Delta Q \) which maximizes \( \lambda_{eg} \). The maximum in \( \lambda_{eg} \) originates from the opposing behavior of \( h_{eg} \) and \( \langle g|\delta H/\delta Q_i|e \rangle \) factors in \( (k, \Delta Q) \) space. A strategy for obtaining large \( \lambda_{eg} \)s should adjust properly small \( \Delta Q \)s in systems with strong multiple bonds (large \( k \)s). This condition appears to be hard to fulfill in experiment. It also emerges that \( \lambda_{eg} \) correlates linearly with \( \sqrt{(k/m)} \). Hence, to maximize \( \lambda_{eg} \) one should build a system of light elements. The results presented here may be useful in the experimental search for high-temperature superconductivity, delimiting the space of element combinations which might be investigated. © 2001 Published by Elsevier Science B.V.

1. Introduction

The vibronic coupling constant (VCC) is an important molecular parameter which describes in a quantitative way the phenomenon of vibrational coupling of electronic states. 2 Interest in VCCs increased substantially when the BCS theory of superconductivity was born [5], because of the fundamental role of electron–phonon coupling in that theory. Although it is clear that the community lost some faith in the explanatory role of classical BCS theory after discovery of high-temperature superconductivity (HTSC) [6] in early ’80s, both theoretical and experimental investigations of VCCs are common in literature [7,8]. Despite many (contradictory) claims by proponents of this or that theory, the HTSC phenomenon remains till today quite mysterious. Also few of the many competing theoretical approaches can be easily translated into chemical language.

Our investigations also have their source in the phenomenon of superconductivity. Although BCS...
theory does not allow a quantitative prediction of the onset and parameters of HTSC, there still exists a qualitative correlation between experimental values of the critical temperature \( T_c \) and those calculated within the BCS theory [9] up to 100 K (see Fig. 1). BCS theory deals with the full polaron coupling problem, including terms that are both diagonal and off-diagonal in the local electronic populations. Since BCS predicts higher \( T_c \)s for larger VCCs, it is reasonable to look systematically for higher values of the VCC in order to obtain a higher \( T_c \) value.

More generally, we are looking for a place for chemical intuition in thinking about HTSC, so as to provide a reasonable direction to the experimental search for new materials.

The general plan of our five-part study, entitled “Chemistry of Vibronic Coupling” is as follows: in this paper (part 1) we show, using a simple model of two harmonic potential wells, how to maximize the VCC \( \lambda \) in the “space” of force constants, normal coordinates and reduced oscillator masses. In forthcoming papers we will then look closer at diagonal and off-diagonal VCCs \( h \) in a space of “chemical parameters” such as the electronegativity and covalent/ionic radii of the elements involved. In part 2 of the series [14] we perform quantum mechanical (QM) calculations of the dynamic diagonal VCC for closed shell diatomics \( \text{MeX} \) (\( \text{Me} = \text{alkali metal or H, X = halogen or H} \)). In part 3 [15] we perform QM computations of the dynamic off-diagonal VCC for mixed-valence and intermediate valence \( \text{Me}_2\text{X} \) systems (\( \text{Me} = \text{alkali metal or H, X = halogen or H} \)). Finally, in part 4 [16] we will focus on both diagonal and off-diagonal VCCs, looking for rules which might help to understand the influence of \( \text{Me} \) and \( \text{X} \) position in the periodic table on the value of VCC. In part 5 of the series [17], we will try to understand VCCs as molecular systems are expanded into solids.

We will be looking to build a bridge between the VCCs and electron-phonon coupling constants. In our simple considerations of the VCC in the context of superconductivity we thus hope to come all the way from simple molecular systems to solids.

2. Methods of calculations

2.1. Types of vibronic coupling constants

There are many types of VCCs (vibronic coupling constants) used. It is therefore necessary to define accurately our notation and point of interest.

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\(^{3}\) For the work of four groups with a chemical and physical orientation see Refs. [10–13].

\(^{4}\) For definitions of \( \lambda/\text{eV} \) and \( \lambda/\text{eV}/\text{Å} \) see Section 2 of this paper.

\(^{5}\) For vibronic coupling in molecules and in solids see Refs. [18–20]; on the role of vibronic coupling for electronic and vibrational dynamics see Refs. [21,22]; for charge transfer processes in condensed media see Refs. [23,24]; on Jahn–Teller effect in molecules and in solid state see Refs. [25–28].
Most often a VCC is expressed in force units, and denoted as $h$. There may be diagonal and off-diagonal VCCs, and linear and nonlinear ones. Among them we will look closer at the dynamic off-diagonal linear VCC ($h_{eg}$) defined as

$$h_{eg}(Q_i) = \langle g | \delta H / \delta Q_i | e \rangle \text{ (typical units meV/Å)}$$

(1)

where $g$ and $e$ are the diabatic electronic wave functions of two vibronically coupled electronic states, and $\delta H / \delta Q_i$ is the derivative of Hamiltonian along the normal coordinate $Q_i$ through which coupling occurs. Usually $g$ is assumed to be the ground state of a system. $h_{eg}$ depends on geometry of a molecule; in this paper we will be interested only in a dependence of $h_{eg}$ on one normal coordinate, $Q_i$.

If $g \equiv e$, then $h_{eg}$ becomes a diagonal linear CC ($h_{ee}$):

$$h_{ee} = \langle e | \delta H / \delta Q_i | e \rangle \text{ (meV/Å).}$$

(2)

The $h_{ee}$ may be thought as a negative force $F_{ee}$ acting on the potential energy surface (PES) of the excited state $e$ along normal coordinate $Q_i$:

$$h_{ee} = -F_{ee}.$$  

(3)

If one determines $h_{ee}$ at the equilibrium geometry of the ground state ($g_0$), then $h_{ee}$ becomes a derivative of the $g \rightarrow e$ excitation energy along $Q_i$, evaluated at $g_0$:

$$h_{ee} = \delta E_{exc} / \delta Q_i \text{ at } g_0.$$  

(4)

This definition of $h_{ee}$ is close to chemical intuition; Eq. (4) says that $h_{ee}$ is large when the energy of $g \rightarrow e$ excitation changes substantially between opposite phases of normal vibration $i$ (extension and contraction of the bond from its ground state equilibrium value). Fig. 2a illustrates definition of $h_{ee}$ given in Eq. (4).

Eq. (4) helps us to understand the cases when $h_{ee} = 0$. A given vibration $i$ has no effect on the electronic excitation energy when the PES minimum of the excited state $e$ is not displaced along coordinate $Q_i$, in comparison with the PES minimum of the ground state $g$ (Fig. 2b). One way this might be realized is when vibration $i$ involves motion of atoms whose atomic orbitals do not contribute to the molecular orbitals involved in the $g \rightarrow e$ transition. An illustration might be an organic molecule consisting of a chromophoric part and a long side aliphatic chain. The vibrations of the aliphatic chain, separated as they are from the chromophore part of a molecule, obviously have no impact on the $g \rightarrow e$ excitation energy.

When is $h_{ee}$ large? Consider the $g \rightarrow e$ transition arising from a HOMO/LUMO transition. $h_{ee}$ will be large for vibrations involving a given $C_a-C_b$ bond stretch when HOMO and LUMO differ by a node across the $C_a-C_b$ bond. It is very likely that a large $C_a-C_b$ bond length difference between the $g$ and $e$ states (and consequently a strong dependence
of the $g \rightarrow e$ excitation energy on the C<sub>a</sub>–C<sub>b</sub> bond length) would be a consequence of such a nodal change (node in HOMO across the C<sub>a</sub>–C<sub>b</sub> bond, no node in LUMO or vice versa). In other words, if during an electronic transition the bond order for a given bond changes much, then only those vibrations $i$ which involve stretching of this bond will have large $h'_{ge}$.

Let us now return for a moment to off-diagonal CC $h'_{ge}$. Looking at its definition (Eq. (1)) one can easily predict when $h'_{ge}$ vanishes. $h'_{ge} = 0$ when:

(i) the molecular vibration $i$ does not have the proper symmetry to couple states $g$ and $e$ or

(ii) the $g \rightarrow e$ transition is spin-forbidden. Of course, there is an additional simple intuitive rule for $h'_{ge}$, similar to that given for $h'_{ee}$:

(iii) among normal vibrational modes which may couple states $g$ and $e$, the largest values of $h'_{ge}$ should be found for modes $i$ involving movement of atoms whose atomic orbitals contribute substantially to MOs engaged in the $g \rightarrow e$ transition. For example, let the $g \rightarrow e$ transition be a $\pi \rightarrow \pi^*$ transition in a large organic molecule. Let us concentrate at a certain C<sub>a</sub>–C<sub>b</sub> bond, such that contributions of $p_z$ ($\pi$) orbitals of C<sub>a</sub> and C<sub>b</sub> carbon atoms to both $g$ and $e$ states are large. Let the contribution of $p_z$ orbital of C<sub>a</sub> be of the same sign in $g$ and $e$, and let the contribution of $p_z$ orbital of C<sub>b</sub> be of the opposite sign in $g$ and $e$. Under such conditions a large coupling constant $h'_{ge}$ should be expected for those normal modes with a significant contribution from a C<sub>a</sub>–C<sub>b</sub> stretch.

As we will show in the following papers, interesting correlations may be found for $h'_{ge}$ and $h'_{ee}$ for a broad range of simple molecules.

The CC which is most important in considerations of superconductivity (usually denoted $\lambda$) is expressed in energy units and defined as

$$\lambda'_{eg} = \langle \lambda'_{eg} \rangle_c = h'_{eg} \langle u_g | Q_i | v_e \rangle \text{ (meV)}$$

(5)

where $u_g$ and $v_e$ are vibrational wave functions for normal mode $i$, in $g$ and $e$ states respectively. The $\langle u_g | Q_i | v_e \rangle$ integral is computed taking $u_g$ with vibrational quantum number equal to zero and full set of $v_e$ (vibrational quantum number varies from 0 to $\infty$). Again, most often $g$ is here the ground and $e$ a certain excited electronic state.

$\lambda'_{eg}$ and $\lambda'_{ee}$ (which is defined in a manner similar to $\lambda'_{eg}$) have energy units. These parameters are central to classical superconductivity explanations, because of the BCS theory [5] relationship:

$$kT_c = 1.14 \hbar \nu_{\text{Deb}} \exp \left( \frac{\lambda}{\lambda N_F} \right)^{-1}$$

(6)

where $k$ is the Boltzmann constant, $T_c$ the critical superconducting temperature, $\nu_{\text{Deb}}$ the cutoff frequency of the phonon spectrum, $\lambda$ the electron–phonon coupling constant in solid decreased by coulombic repulsion of electrons, and $N_F$ the density of states at the Fermi level. The product $\lambda N_F$ is often called the pairing potential, since it controls the condensation of electrons into boson pairs. In other words, phonons open energy gaps at the Fermi level (the magnitude of the gaps may vary for different vibrations of the lattice). For us it is essential to note that a large electron–phonon coupling constant $\lambda$ leads to a high superconducting transition temperature $T_c$. The present paper is devoted to $\lambda'_{eg}$, a counterpart of BCS $\lambda$ in molecular systems.

The remaining kind of CC which is often used is a dimensionless one (denoted most often as $g'_{eg}$) and defined as

$$g'_{eg} = \left[ \frac{1}{\hbar \omega_i} \right] \lambda'_{eg}$$

(1)

where $\hbar \omega_i$ is the energy of vibration $i$. Definition of $g'_{eg}$ is analogous to that given in Eq. (7). While we are not directly interested in the $g'_{eg}$ and $g'_{ee}$, they are widely used in resonance Raman studies [29], theory of CT complexes [30] and in the Marcus theory of electron transfer [31] when analyzing contributions from various vibrations to distortion of a molecule upon electron transfer (most often $g'_{ee}$ is point of interest in studies based on so-called crude Born–Oppenheimer approximation).

So far we have introduced here the coupling constants for a single normal mode $i$ ($h'_{ee}$, $h'_{eg}$, $\lambda'_{eg}$, $\lambda'_{ee}$, $g'_{eg}$, $g'_{ee}$). These are linear CCs. There are cases, when CCs of higher order than linear should be considered. The simplest quadratic off-diagonal CC is defined as

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6 Both diagonal and off-diagonal vibronic coupling constants enter BCS considerations as mentioned above.
\[ h_{eg}^i = \langle g | \delta^2 \hat{H} / \delta Q_i \delta Q_j | e \rangle \ (\text{meV}/\AA^2), \]  
(8) 

with its diagonal counterpart 
\[ h_{eg}^{ii} = \langle e | \delta^2 \hat{H} / \delta Q_i \delta Q_j | e \rangle \ (\text{meV}/\AA^2). \]  
(9) 

Now, \( i \) and \( j \) are two normal vibrational modes. In case \( i \neq j \), \( h_{eg}^i \) describes vibronic coupling of \( e \) and \( g \) states through an \( i \) and \( j \) combination mode. When \( i = j \), \( h_{eg}^{ii} \) describes vibronic coupling of \( e \) and \( g \) through \( i \)'s first overtone. Of course, quadratic \( \lambda_{eg}^{ii} \) and \( \lambda_{eg}^{ij} \) may be easily derived from both \( h_{eg}^{ii} \) and \( h_{eg}^i \), respectively. In the present and forthcoming papers [14–16] in our series “Chemistry of vibronic coupling” we will not consider quadratic and higher CCs.

As noted earlier, our main interest will be in \( h_{eg}^i \), \( h_{eg}^{ii} \), and \( \lambda_{eg}^i \) (especially when a \( g \rightarrow e \) transition has charge-transfer character). The central focus of this paper is \( \lambda_{eg}^i \). \(^7\)

The literature in this field is diverse, traversing chemistry and physics. There are many current nomenclatures in place for \( h \), \( g \), and \( \lambda \). We have taken time here, with apologies to the experts in the field, to delineate clearly the relationships between the different measures of vibronic coupling.

Let us present now the simple model used for \( \lambda_{eg}^i \) calculations.

### 2.2. Model for calculations of the \( \lambda_{eg}^i \)

Imagine two electronic states \( g \) and \( e \) described by harmonic potential curves along coordinate \( Q_i \) (Fig. 3a). We introduce the variables \( k, \Delta Q, c, \) and \( m \). \( k \) has physical meaning of a force constant for vibration \( i \) in both \( e \) and \( g \) states, \( \Delta Q \) is the displacement between the minima of \( e \) and \( g \) states along \( Q_i \), \( c \) is the vertical (energy) displacement between the minima of \( e \) and \( g \) states, and \( m \) is a reduced mass for vibration \( i \). In our diabatic model we assume, similarly to Marcus [33], that the force constants in states \( g \) and \( e \) are the same. \(^8\) When \( c = 0 \) we have the case of a degenerate double-minima potential well, realized for asymmetric mixed-valence compounds (see Fig. 3b). We want to find \( \lambda_{eg}^i \) according to Eq. (5), varying \( k, \Delta Q, c, \) and \( m \) as widely as possible. One immediately notices that parameter \( c \) does not change the value of \( \lambda_{eg}^i \) (neither the \( h_{eg}^i \) nor the \( \langle u_g | Q_i | v_e \rangle \) term) in our model (although it contributes to the \( g \rightarrow e \)

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\(^7\) We consider here a special case when the same vibration is Herzberg–Teller active and involved in a geometry change upon electronic excitation. In this context note an opposite case, when a Herzberg–Teller active mode does not form progression in the electronic spectrum, and the progression-forming frequencies do not effect vibronic perturbations. See an interesting contribution on the phenanthrene 3400 Å system in Ref. [32].

\(^8\) This approximation is usually fulfilled with 10% accuracy, but deviations as big as ±30% are known. We will discuss later the qualitative impact of these deviations on the value of \( \lambda \), while now we will remain within the above assumption.
excitation energy). Thus, we will exclude parameter $c$ from the space of variables, reducing it to $k$, $\Delta Q$ and $m$. Phenomenologically, these three parameters fully describe $\beta'_{eg}$ in any molecular system within a diabatic harmonic potential model.

We have performed a scan of values of the VCC $\beta'_{eg}$ in the space of the above molecular parameters. For this purpose a short program in the Python programming language has been written. Our algorithm computes independently the $h'_{eg}$ term and $\langle u_{eg}|Q|v_{e}\rangle$ term. The $h'_{eg}$ term is simply [34]

$$h'_{eg} = k\Delta Q,$$

(10)

which requires no integration and is obviously $m$-independent.

The $\langle u_{eg}|Q|v_{e}\rangle$ term is found by a numerical integration procedure. The algorithm used was Romberg's extension to the trapezoidal rule for better computational efficiency. A vibrational wave function for a quantum oscillator is

$$\Psi_{v}(Q) = N_v H_v(y) \exp\left(-y^2/2\right)$$

(11)

where

$$N_v = \left\{2v!\right\}^{-1/2}$$

(12)

is the normalization factor.

$$H_v(y) = (-1)^v \exp(y^2) dv^v \exp(-y^2) / dy^v$$

(13)

is Hermite's polynomial and

$$y = [m \omega_i 2\Pi/k]^{1/2} Q,$$

(14)

$$\omega = (k/m)^{1/2}$$

(15)

where $\omega_i/2\Pi$ is the frequency of vibration $i$, and $v$ is the vibrational quantum number.

Our algorithm computes the $\langle u_{eg}|Q|v_{e}\rangle$ term taking up to 15th order Hermite polynomials. We have observed that due to the normalization factor $N_v$ (strongly decreasing with $v$) the contribution from higher orders than the 15th is negligible. The integration limits were usually $(-7, +7)$ bohrs with a 0.01 bohr grid, providing fast convergence. For large values of $k$ and small values of $\Delta Q$, huge integration limits were not necessary. Hence, smaller integration limits of $\pm 3$ to 5 bohrs were used. Finally, the $\langle u_{eg}|Q|v_{e}\rangle$ term was multiplied by $h'_{eg}$ to get $\beta'_{eg}$.

Our calculations were performed in atomic units of $h$, atomic mass units, hartrees and bohrs. In these units: $k = 1$ hartree/bohr$^2$ = 1556.7 N/m = 15.567 mDyne/Å. Numerical results are shown in Table 1.

### Table 1

<table>
<thead>
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<th>$m = 1$</th>
<th>$m = 10$</th>
<th>$m = 100$</th>
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<tr>
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<td>$\Delta Q$ (bohr)</td>
<td>$h$ (hartree/bohr)</td>
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3. Results and discussion

Fig. 4 presents a plot of $\beta'_{eg}$ and its components: $\langle u_{eg}|Q|v_{e}\rangle$ and $h'_{eg}$ as a function of $\Delta Q$ for $k = 5$ and $m = 1$. This plot is central to our considerations. Its main features can be easily deduced without calculations. Indeed, this is how we really came a long way toward understanding of $\beta'_{eg}$, before any computations were performed.

It may be seen in Fig. 4 that there appears a maximum in $\beta'_{eg}$ at about 0.25 bohr. This maxi-

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[35] Analytical formulas have been obtained in Ref. [35].
maximum originates from the opposing behavior of $h^{i}_\text{eg}$ (which, since $h^{i}_\text{eg} = k\Delta Q$, grows with increasing $\Delta Q$) and $\langle u_{\text{eg}} | Q | v_{\text{e}} \rangle$ (which decreases with increasing $\Delta Q$). The product of these two terms has a maximum along $\Delta Q$. Very similar plots (not shown here) may be obtained for $\lambda^{i}_\text{eg}$ and its components: $\langle u_{\text{eg}} | Q | v_{\text{e}} \rangle$ and $h^{i}_\text{eg}$ as a function of $k$ for $\Delta Q$, $m = \text{const}$. Again, for small values of $k$ ($k \approx 0$), the overall $\lambda^{i}_\text{eg}$ is close to 0, due to the small $h^{i}_\text{eg}$ term. For large values of $k$, the $\langle u_{\text{eg}} | Q | v_{\text{e}} \rangle$ term is now very small, giving rise to a small $\lambda^{i}_\text{eg}$. Again, there is some optimal value of $k$, yielding maximum $\lambda^{i}_\text{eg}$. The existence of a maximum in $\lambda^{i}_\text{eg}$ in Fig. 4 is very interesting in the context of superconductivity. It means that one needs to find an optimal value of $\Delta Q$ (hereafter called $\Delta Q_{\text{opt}}$) for a given $k$ and $m$, or an optimal value of $k$ (hereafter called $k_{\text{opt}}$) for a given $\Delta Q$ and $m$, in order to attain a maximum value of the coupling constant $\lambda^{i}_\text{eg}$.

Let us now plot the $(\Delta Q, k)$ points providing maximum $\lambda^{i}_\text{eg}$ for three different values of $m$ ($m = 1$ amu, 10 amu, 100 amu). As it may be seen in Fig. 5, the position of $\Delta Q_{\text{opt}}$ is a monotonic and decreasing function of $k$ for all three reduced masses. The necessity of $\Delta Q$ tuning for given value of $ks$ in order to maximize $\lambda^{i}_\text{eg}$ may be easily understood. For very steep parabolas describing the PES of electronic states $g$ and $e$, one needs to provide small $\Delta Q_{\text{opt}}$ to have $\langle u_{\text{eg}} | Q | v_{\text{e}} \rangle$ large enough.

On the other hand, it is necessary to separate the minima of shallow parabolas to obtain large $h^{i}_\text{eg}$ (and hence attain large $\lambda^{i}_\text{eg}$). Interestingly, the position of “optimal” $\Delta Q_{\text{opt}}$ for a given $k$ varies with $m$. At a given $k$, the larger $m$, the smaller $\Delta Q_{\text{opt}}$. Or, alternatively, at given $\Delta Q$, the larger $m$, the smaller $k_{\text{opt}}$. The hyperbolic-like behavior of optimal (i.e., those providing highest $\lambda^{i}_\text{eg}$) $(\Delta Q, k)$ points may be understood considering four simple relationships:

$$\lambda^{i}_\text{eg} = 0 \quad \text{for } k = 0 \quad \text{(ordinate axis in Fig. 5)},$$

(16a)
\[ \lambda_{eg}^{j} = 0 \quad \text{for} \Delta Q = 0 \quad \text{(abscissa axis in Fig. 5)}, \]

\[(16b)\]

\[ \lambda_{eg}^{j} = 0 \quad \text{for} \ k \to \infty \quad \text{and} \quad \Delta Q \to \infty, \]

\[(16c)\]

\[ \lambda_{eg}^{j} \quad \text{should be a continuous function of} \ k \quad \text{and} \ \Delta Q. \]

\[(16d)\]

Computational data suggest that with simultaneous \( k \) and \( \Delta Q \) increase, the \( \langle u_{eg} \vert Q \vert v_{c} \rangle \) term goes to zero faster than the \( h_{eg}^{j} \) term goes to infinity (Eq. (16c)).

Fig. 5 does not tell us about \( \lambda_{eg}^{j} \) values at “optimal” \((k, \Delta Q)\) points. Consider such \( \lambda_{eg}^{j} \), plotted as a function of \( \sqrt{k/m} \) (Fig. 6).

As may be seen in Fig. 6, \( \lambda_{eg}^{j} \) is a linear function of \( \sqrt{k/m} \) for “optimal” \((k, \Delta Q)\) points (of course, it is not a linear function of \( \sqrt{k/m} \) for any \((k, \Delta Q)\) points). The largest \( \lambda_{eg}^{j} \) of 3.7 hartree (within the space of \( k, m \) and \( \Delta Q \) monitored by us) is reached for \( k = 1000 \) hartree/bohr\(^2 \approx 15.6 \times 10^3 \) mDyne/\( \AA \), for \( m = 1 \) amu and at \( \Delta Q_{opt} \) (about 0.04 bohr). Of course, 1000 hartree/bohr\(^2 \) is a force constant value which cannot be reached by any molecular or extended system. It is two orders of magnitude larger than the force constant for the nitrogen molecule N\(_2\) (≈3 hartree/bohr\(^2\)). That extreme upper \( k \) limit was not realistic, but chosen only to illustrate clearly the trend for \( \lambda_{eg}^{j} \) which holds regardless of the \((k, \Delta Q)\) – space probing. Let us proceed, limiting ourselves to a reasonable space of \( ks \) in the range from 0 to 5 hartree/bohr\(^2\). For a typical chemical system with \( k = 1 \) hartree/bohr\(^2 \) and \( m = 10 \) amu, \( \lambda_{eg}^{j} \) will decrease to 0.037 hartree (about 1 eV) for “optimal” \( \Delta Q \). For “nonoptimal” \( \Delta Q \), values of \( \lambda_{eg}^{j} \) will be smaller than this.

There is one more question that begs to be answered: can \( h_{eg}^{j} \) be a monotonic indicator of large \( \lambda_{eg}^{j} \)? Let us put the problem in other way: if \( k \) increases and \( \Delta Q \) simultaneously decreases (\( k \) and \( \Delta Q \) are optimal for each other), what happens to the \( \lambda_{eg}^{j} \) values? The answer to this question is given in Fig. 7.

As may be seen in Fig. 7, if optimal \((k, \Delta Q)\) are provided, the increase in \( h_{eg}^{j} \) is connected with

![Fig. 6. Plot of \( \lambda_{eg}^{j} \) values at “optimal” \((k, \Delta Q)\) points as a function of \( \sqrt{k/m} \).](image)

![Fig. 7. Illustration of the \( \lambda_{eg}^{j} \) vs \( h_{eg}^{j} \) monotonic relationship for three masses \((m = 1, 10, 100 \text{ amu})\) at \((k, \Delta Q)\) points optimal for given \( h_{eg}^{j} \).](image)
simultaneous monotonic (although less than linear) increase of \( \lambda_{eq}^i \). Let us summarize the results obtained. The perspectives for maximizing the coupling constant \( \lambda_{eq}^i \) are as follows:

(i) there exists a maximal value of \( \lambda_{eq}^i \) which may be found for a given force constant \( k \) by providing the appropriate \( \Delta Q_{\text{opt}} \). \( \Delta Q_{\text{opt}} \) decreases with \( k \) increasing.

(ii) \( \lambda_{eq}^i \) may be maximized by increasing the \( k/m \) ratio with simultaneous adjustment of \( \Delta Q \).

(iii) \( \lambda_{eq}^i \) may be maximized for given \( m \) by increasing \( h_{eq}^i \), but \( k \) should be precisely adjusted to \( \Delta Q \).

These rules may be translated into chemical language as follows:

(iv) large values of \( \lambda_{eq}^i \) in mixed-valence molecular systems should be sought for in systems with strong multiple bonds (large \( k \)) built of light elements (small \( m \)). The \( \Delta Q \) should be precisely adjusted for a given \( (k,m) \) pair. The larger the expected values of \( \lambda_{eq}^i \), the greater precision in \( \Delta Q \) tuning is necessary.

One can see two serious problems in applying the qualitative understanding reached, even for molecules. These are connected with the necessity of precise \( \Delta Q \) adjustment for large \( k \). Under- or overestimation of \( \Delta Q \) results in a strong decrease of \( \lambda_{eq}^i \). The problems are as follows:

(1) Many molecules with large \( k \) \(^{10}\) prefer to be symmetric. Exceptions from a “self-symmetrization” of the system for large \( k \) are only found among molecules with large \( h_{eq}^i \), such as symmetric linear \( \text{F}_3 \) or \( \text{F}_2\text{H} \) radicals [16]. Such molecules are, however, extremely unstable toward decomposition [16].

(2) Another complication is hidden in the real adiabatic (and not diabatic, as previously assumed) character of the \( g \) and \( e \) states, which mix, creating two nondegenerate states: the real ground and excited state of a system (see next section). According to the simplest theory using adiabatic potentials [36], strong adiabaticity influences \( \Delta Q \) in a major way, usually leading to symmetrization of a molecule along \( Q \). Given adiabaticity as one more independent parameter, it is not easy to guess and provide the “optimum” value of \( \Delta Q \) for given molecule.

These examples show how difficult it will actually be to design large \( \lambda_{eq}^i \) by playing with \( \Delta Q \).

Our observations of the existence of optimal \( \Delta Q \) for given \( k \) have an interesting counterpart in studies of high-temperature superconductors. As experimental \( T_c \) vs doping \( (x) \) and \( T_c \) vs external pressure \( (p) \) curves show, there exists an optimal level of doping and an optimal external pressure applied which allow \( T_c \) maximization [37,38]. Either too small or too large values of \( x \) and \( p \) strongly influence bond distances and lead to disappearance of the HTSC phenomenon. On the other hand, experimental data (mainly for the well-studied cuprates [39,40]) indicate a strong correlation of HTSC with lattice instability and phase transitions in these complex solid state systems.

Let us now briefly discuss the qualitative impact of deviations from diabaticity and harmonicity on final value of \( \lambda_{eq}^i \).

3.1. The effects of deviations from diabaticity and harmonicity on \( \lambda_{eq}^i \)

In the simple model used, we have assumed harmonicity of the vibrations in \( g \) and \( e \) states along \( Q \) (with force constants equal in both states, \( k_e = k_g \)) and diabaticity (PESs for states \( g \) and \( e \) cross at \( Q = 0 \), see Fig. 3b). We would like to discuss now briefly and in a qualitative way the impact of breakdown of these assumptions on the value of \( \lambda_{eq}^i \).

(i) What if \( k_e \neq k_g \)? Since we decided to look for large \( \lambda_{eq}^i \)'s among systems with strong multiple bonds (providing large \( k \)), we should not be bothered by eventual breakdown of the \( k_e = k_g \) assumption. To demonstrate this, consider a typical mixed-valence (MV) system of type \( \{M^{n^+} - A^{m^-} - M^{(n+1)+}\} \). Given the same \( \sigma \) skeleton in two “units” differing by one electron \( (M^{n^+} - A^{m^-} \) and \( A^{m^-} - M^{(n+1)+}) \), the differences in stretching force constants for the above units originate exclusively from the partial \( \pi \) bonding. Since \( \pi \) bonds are

\(^{10}\) We mean here \( k \), which has been used by us to describe curvature of parabolas in a diabatic potential model, and not a real force constant for antisymmetric stretch of \( \text{F}_3 \) or \( \text{F}_2\text{H} \). Obviously the latter is imaginary for both systems.
much weaker than $\sigma$ bonds, stretching force constants for the above units will not differ much. Hence, our assumption of $k_e = k_g$ will be violated only slightly.

(ii) What if vibrations are not harmonic? The effect of anharmonicity of vibrations on our model is shown in Fig. 8a.

It seems that anharmonicity has a double impact on $\lambda_{eg}^t$, through $h_{eg}^t$ and also through $\langle u_e | Q | v_e \rangle$. While anharmonicity increases $h_{eg}^t$ (by comparison with harmonic case), it diminishes the $\langle u_e | Q | v_e \rangle$ term. The result of the interplay of $h_{eg}^t$ and $\langle u_e | Q | v_e \rangle$ (though the influence of these two seems to cancel to some extent) is difficult to deduce. And, in experiment, is difficult to control. More exact studies (using Morse potentials for example) might be performed in order to determine quantitatively the role of anharmonicity for $\lambda_{eg}^t$.

(iii) What if the system is adiabatic? The effect of increasing adiabaticity is illustrated in Fig. 8b [41]. Among factors discussed so far, adiabaticity (measured by electronic coupling parameter $\Lambda$ [34,36]) undoubtedly has the strongest impact on $\lambda_{eg}^t$. Again, its role is not easily quantified. Adiabaticity influences values of $h_{eg}^t$, $\Delta Q$ and $\langle u_e | Q | v_e \rangle$, i.e. $\lambda_{eg}^t$ and $\Lambda$ are not independent parameters. In our opinion, the most significant influence of increasing adiabaticity on $\lambda_{eg}^t$ is connected with the tendency for symmetrizing a molecule even for large $h_{eg}^t$ (a mixed-valence system becomes an intermediate-valence system). This means that large $\lambda_{eg}^t$ may be also hidden in symmetric systems, contrary to our predictions based on a simplistic diabatic potential model.

4. Conclusions

Using a simple diabatic model of two equivalent electronic states with harmonic PESs, we analyze values of the dynamic off-diagonal VCC ($\lambda_{eg}^t$) as a function of three parameters: force constant ($k$), reduced oscillator mass ($m$) and displacement between two minima along the normal coordinate of a coupling mode $Q_1 (\Delta Q)$. We show that for each $k$ there is only one $\Delta Q$ which maximizes $\lambda_{eg}^t$. Existence of a maximum in the $\lambda_{eg}^t$ originates from the opposing behavior of $h_{eg}^t$ and $\langle g | \delta H / \delta Q | e \rangle$ factors in $(k, \Delta Q)$ space.

In searching for large $\lambda_{eg}^t$ we are then led to adjusting properly small $\Delta Q$s in systems with strong multiple bonds (large $k$s). It also emerges that $\lambda_{eg}^t$ correlates linearly with $\sqrt{k/m}$. Hence, one should build system of light elements so to maximize $\lambda_{eg}^t$. However, these conditions are very hard to realize experimentally, because real systems with large $k$s either have a tendency (a) toward symmetrization along $Q_1$, or (b) to chemical decomposition. $\Delta Q$ and $k$ are not independent parameters, as well.

The results presented here may be useful in the experimental search for HTSC, in delimiting the space of element combinations which should be investigated. Of course, superconductivity is a very complex solid state physical phenomenon. It cannot be explained exclusively by a simple diabatic, harmonic potential model such as that we used in our simulations. This is why in parts 2, 3 and 4 of this series we will computationally examine dynamic linear VCCs in real QM molecular systems.

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