

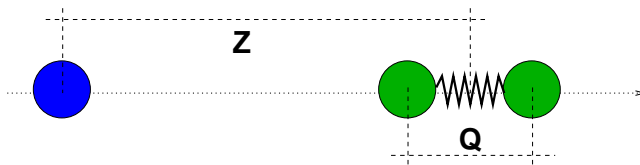
Vibrational Sudden Approximation

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1 A simple model

1.1 Time independent picture

Let's consider a very simple two dimensional model: the linear collision of an atom and a diatomic molecule.



With a simple linear transformation of the coordinate Z (the distance between the incident atom and the center of mass of the molecule) and of the coordinate Q (the internal degree of freedom of the molecule) [see ref Bowman79], we can define the dimensionless mass scaled coordinates z and q such that the Hamiltonian of the system is

$$H(z, q) = -\frac{1}{2}\partial_z^2 - \frac{1}{2}\partial_q^2 + V_{vibr}(q) + V_{scatt}(z, q) \quad (1)$$

where V_{vibr} is the potential for the vibrations of the diatomic molecule and V_{scatt} is the atom-molecule interaction.

When the atom is far from the molecule ($z \rightarrow \infty$), V_{scatt} is negligible and a convenient set of eigenstates for this system is made of the product functions

$$\langle zq | np \rangle = \chi_n(q) e^{ipz} \quad n = 0, 1, \dots \quad p \in [-\infty; +\infty]$$

where $\vartheta_p(z)$ is a plane wave of momentum p and $\chi_n(q)$ is the n -th eigenfunction of the one dimensional molecular Hamiltonian

$$\left(-\frac{1}{2}\partial_q^2 + V_{vibr}(q) \right) \chi_n(q) = E_n \chi_n(q)$$

We label the eigenstates χ_n with the index n assuming that the potential admits only bound states. If the potential allows the molecule to dissociate,

also continuous states are possible. However in such case our discussion can be generalized in a straightforward manner¹.

Let's consider the scattering states for our model system

$$|np\pm\rangle = \Omega_{\pm} |np\rangle$$

These states represent an atom with momentum p that collide with a molecule in the n -th vibrational state.

Without any approximation, we can write the scattering states as the product

$$\langle zq | np\pm\rangle = \chi_n(q) \varphi_{np}^{\pm}(z, q)$$

Since the scattering event couples different vibrational states of the target molecule, $\langle zq | np\pm\rangle$ is not a simple product state, and the function φ_{np} still depends on q .

The Vibrational Sudden Approximation consists in assuming that the function $\varphi_{np}(z, q)$ is a slowly varying function of the vibrational coordinate q , i.e.

$$\frac{\partial^2}{\partial q^2} [\chi_n(q) \varphi_{np}^{\pm}(z, q)] \approx \varphi_{np}^{\pm}(z, q) \partial_q^2 \chi_n(q) \quad (2)$$

The physical meaning of this assumption will be discussed later, from a time dependent point of view. Now we want to derive an equation to compute $\varphi_{np}(z, q)$. The scattering states are eigenfunctions of the Hamiltonian operator

$$\left(-\frac{1}{2} \partial_z^2 - \frac{1}{2} \partial_q^2 + V_{vibr}(q) + V_{scatt}(z, q) - \left(E_n + \frac{p^2}{2} \right) \right) \chi_n(q) \varphi_{np}^{\pm}(z, q) = 0$$

where the eigenvalue can be found applying the intertwining relation.

Applying the VSA approximation we get

$$\begin{aligned} \left(-\frac{1}{2} \partial_z^2 + E_n + V_{scatt}(z, q) - \left(E_n + \frac{p^2}{2} \right) \right) \varphi_{np}^{\pm}(z, q) &= 0 \\ \left(-\frac{1}{2} \partial_z^2 + V_{scatt}(z, q) - \frac{p^2}{2} \right) \varphi_{np}^{\pm}(z, q) &= 0 \end{aligned} \quad (3)$$

This part of the scattering wavefunction is just a solution of a simpler one dimensional problem, in which the scattering potential depends parametrically on q . We define the VSA Hamiltonian as the the hamiltonian of this lower dimensional system

$$H_{VSA}(q, z) = -\frac{1}{2} \partial_z^2 + V_{scatt}(z, q) \quad (4)$$

¹If the vibrational coordinate is highly excited and the continuum states are populated, the assumption of Vibrational Sudden Approximation (Eq. (2)) is most unlikely to hold. This however has nothing to do with the present mathematical discussion but with the specific physical properties of the system.

The VSA hamiltonian is a family of one dimensional system, in which the solution is parametrically dependent of the coordinate q . Hence, instead of dealing with one single two dimensional problem, we now can solve an infinite number of simpler one dimensional problems with potential $V^q(z) = V_{scatt}(z, q)$.

In the following we will use the semicolon to point out that the dependence on q is parametrical. From the same equation, we can see that the solution is independent on the vibrational state n . From now on we will drop the n label from the wavefunction. In conclusion, the scattering state in the VSA is

$$\langle zq | np \pm \rangle = \chi_n(q) \varphi_p^\pm(z; q)$$

Consequently, the scattering matrix can be written as

$$\begin{aligned} S(pn \leftarrow p'm) &= \langle pn- | mp'+ \rangle = \\ &= \int dq \int dz \langle pn- | zq \rangle \langle zq | mp'+ \rangle = \\ &= \int dq \int dz (\chi_n(q) \varphi_p^-(z; q))^* (\chi_m(q) \varphi_{p'}^+(z; q)) = \\ &= \int dq \chi_n^*(q) \left[\int dz (\varphi_p^-(z; q))^* \varphi_{p'}^+(z; q) \right] \chi_m(q) \end{aligned}$$

In square parentheses, we can recognize the q dependent S matrix for the scattering problem corresponding to the VSA Hamiltonian

$$S(pn \leftarrow p'm) = \int dq \chi_n^*(q) S^{\text{VSA}}(p \leftarrow p'; q) \chi_m(q)$$

1.2 Time dependent picture

To understand what are the implications of the VSA from a dynamical point of view, let's analyze the assumption of Eq. (2) from a time dependent point of view.

Let's consider an initial wavefunction $\chi_n(q) \varphi(z)$ which evolves in time according to the full hamiltonian of Eq. (1)

$$\psi(q, z, t) = U_t \chi_i(q) \varphi(z)$$

The VSA consists in assuming that the coupling potential commutes with the vibrational Hamiltonian $H_q = -\frac{1}{2} \frac{\partial^2}{\partial q^2} + V_{vibr}(q)$

$$[H_q, V_{scatt}] \approx 0 \quad (5)$$

so that the vibrational states is not perturbed during the propagation. In fact under such assumption the vibrational hamiltonian commutes with the VSA hamiltonian and the evolution operator can be split according to

$$U_t = \exp(-iHt) \approx \exp(-iH_q t) \exp(-iH_{\text{VSA}} t)$$

Hence the evolving state in the VSA is

$$\psi(q, z, t) = \exp(-\imath H_q t) \chi_i(q) \exp(-\imath H_{VSA} t) \varphi(z)$$

i.e. it can be written as a simple product of two functions, each solution of a one dimensional problem. The part depending just on q , $\exp(-\imath H_q t) \chi_i(q)$, is a stationary eigenstate, representing the vibration of the molecule, unperturbed by the scattering event. The other factor $\exp(-\imath H_{VSA} t) \varphi(z)$ is a simple wavepacket, that evolves according to a potential which just parametrically depends on the vibrational coordinate q .

Now we can examine the assumption of Eq. (5) with greater detail. The part of H_q which does not commute with the coupling potential is the kinetic energy part, since multiplicative operators always commute. Explicitly, the commutation relation can be written as

$$\partial_q^2 V_{scatt}(z, q) \psi(q, z) \approx V_{scatt}(z, q) \partial_q^2 \psi(q, z) \quad (6)$$

which means that the coupling potential is a slowly varying function of q with respect to the vibrational eigenstates. By applying the derivation rule, we find that the commutator (and hence the error) is proportional to

$$\varepsilon \sim (\partial_q^2 V_{scatt}(z, q)) \psi(q, z) + 2 (\partial_q V_{scatt}(z, q)) (\partial_q \psi(q, z))$$

For small displacement of the vibrational coordinate, we can further assume the coupling potential to be a linear function of q

$$V_{scatt} = \kappa q f(z)$$

The VSA error then becomes

$$\varepsilon \sim 2\kappa f(z) (\partial_q \psi(q, z))$$

For each (q, z) point, the approximation is satisfied if

1. the “local” velocity of the oscillator is small (compared to the scattering degree of freedom)

$$\partial_q \psi(q, z) \approx 0$$

2. the coupling coefficient is small (compared to the total potential of the system)

$$\kappa f(z) \approx 0$$

2 Vibrational Sudden Approximation in molecule surface scattering

Now let’s turn our attention to the scattering of molecules on surface. If we consider the six degree of freedom of the molecule and one additional vibrational degree of freedom for the surface, the Hamiltonian can be written as

$$H = -\frac{1}{2M} \nabla_{\mathbf{R}}^2 - \frac{1}{2M} \nabla_{\mathbf{r}}^2 - \frac{1}{2\mu} \partial_Q^2 + V_{6D}(\mathbf{R}, \mathbf{r}) + V_{coupling}(\mathbf{R}, \mathbf{r}, Q) + V_{vib}(Q)$$

We have split the total 7D potential in three terms: V_{6D} is the interaction of the molecule with the static equilibrium surface, V_{vibr} is the vibrational potential for the surface degree of freedom and $V_{coupling}$ is the coupling between the molecule and the surface degrees of freedom.

We can apply the Vibrational Sudden Approximation to the vibrational degree of freedom of the surface:

$$\left[-\frac{1}{2\mu} \partial_Q^2 + V_{vib}, V_{coupling} \right] \approx 0$$

The VSA Hamiltonian will be

$$H_{VSA}(\mathbf{R}, \mathbf{r}; Q) = -\frac{1}{2M} \nabla_{\mathbf{R}}^2 - \frac{1}{2M} \nabla_{\mathbf{r}}^2 + V_{6D}(\mathbf{R}, \mathbf{r}) + V_{coupling}(\mathbf{R}, \mathbf{r}, Q)$$

As in the case of the simple two dimensional problem, this Hamiltonian is a scattering problem with one less degree of freedom and parametrically dependent on the vibrational coordinate Q . The VSA scattering matrix will be

$$S^{VSA}(\mathbf{f} \leftarrow \mathbf{i}; Q)$$

where the indices i and f labels the initial and final state of the scattered molecule ². Labelling the initial and final vibrational state of the surface with μ and μ' , the 7D scattering matrix in the VSA is given by

$$S(\mathbf{f} \mu' \leftarrow \mathbf{i} \mu) = \int dQ \chi_{\mu'}^*(Q) S^{VSA}(\mathbf{f} \leftarrow \mathbf{i}; Q) \chi_{\mu}(Q)$$

where $\chi_{\mu}(Q)$ and $\chi_{\mu'}(Q)$ are two eigenfunctions of the vibrational hamiltonian

$$H_{vib} = -\frac{1}{2\mu} \partial_Q^2 + V_{vib}(Q)$$

The scattering probability, summed over the final vibrational state of the surface is

$$P_{scatter}(\mathbf{f} \leftarrow \mathbf{i} \mu) = \sum_{\mu'} |S(\mathbf{f} \mu' \leftarrow \mathbf{i} \mu)|^2$$

In the VSA, this sum can be simplified according to

$$\begin{aligned} \sum_{\mu'} |S(\mathbf{f} \mu' \leftarrow \mathbf{i} \mu)|^2 &= \sum_{\mu'} S^*(\mathbf{f} \mu' \leftarrow \mathbf{i} \mu) S(\mathbf{f} \mu' \leftarrow \mathbf{i} \mu) = \\ &= \sum_{\mu'} \left(\int dQ \chi_{\mu'}^*(Q) S^{VSA}(\mathbf{f} \leftarrow \mathbf{i}; Q) \chi_{\mu}(Q) \right)^* \int dQ' \chi_{\mu'}^*(Q') S^{VSA}(\mathbf{f} \leftarrow \mathbf{i}; Q') \chi_{\mu}(Q') = \end{aligned}$$

²In detail, \mathbf{i} will identify the initial momentum \mathbf{p} and the initial rovibrational state of the molecule $\nu j m_j$. The final index \mathbf{f} will specify the quantum numbers of the diffraction channel $n_X n_Y$ and the rovibrational state of scattered molecule $\nu' j' m'_j$. The final momentum along Z is fixed by energy conservation.

$$\int dQ \int dQ' \sum_{\mu'} \chi_{\mu'}(Q) \chi_{\mu'}^*(Q') (S^{\text{VSA}}(\mathbf{f} \leftarrow \mathbf{i}; Q))^* S^{\text{VSA}}(\mathbf{f} \leftarrow \mathbf{i}; Q') \chi_{\mu'}^*(Q) \chi_{\mu'}(Q')$$

From the completeness of the vibrational states $\chi_{\mu'}$

$$\sum_{\mu'} \chi_{\mu'}(Q) \chi_{\mu'}^*(Q') = \delta(Q - Q')$$

In conclusion, the (molecule) state resolved reaction probability is given by the average of the VSA scattering probability, with a weight which is given by the square of the initial vibrational eigenfunction

$$P_{\text{scatter}}(\mathbf{f} \leftarrow \mathbf{i}; \mu) = \int dQ |S^{\text{VSA}}(\mathbf{f} \leftarrow \mathbf{i}; Q) \chi_{\mu}(Q)|^2$$

Note that with a knowledge of $S^{\text{VSA}}(\mathbf{f} \leftarrow \mathbf{i}; Q)$, the scattering probability can be computed for any initial state just by changing the vibrational eigenstate in the integral.

From a practical point of view, we can use this equation by computing the VSA scattering matrix on a suitable grid $\{Q_n\}$ and by performing the integration with a quadrature rule

$$P_{\text{scatter}}(\mathbf{f} \leftarrow \mathbf{i}; \mu) = \sum_n |S^{\text{VSA}}(\mathbf{f} \leftarrow \mathbf{i}; Q_n) \chi_{\mu}(Q_n)|^2 w_n$$

where the coefficients w_n are the weights of the quadrature rule.

From the state resolved scattering probability, the reaction probability can be computed by

$$P_{\text{react}}(\mathbf{i}, \mu) = 1 - \sum_{\mathbf{f}} P_{\text{scatter}}(\mathbf{f} \leftarrow \mathbf{i}; \mu)$$

The reaction probability then become

$$\begin{aligned} P_{\text{react}}(\mathbf{i}, \mu) &= 1 - \int dQ |\chi_{\mu}(Q)|^2 \sum_{\mathbf{f}} |S^{\text{VSA}}(\mathbf{f} \leftarrow \mathbf{i}; Q)|^2 = \\ &= 1 - \int dQ |\chi_{\mu}(Q)|^2 (1 - P_{\text{react}}^{\text{VSA}}(\mathbf{i}, Q)) = \int dQ |\chi_{\mu}(Q)|^2 P_{\text{react}}^{\text{VSA}}(\mathbf{i}, Q) \end{aligned}$$

As for the scattering probability, the reaction probability can be computed simply averaging the reaction probability with weights equal to the square of the initial vibrational eigenfunction.

In the last formula the reaction probability depends on the vibrational state of the surface. If we assume the surface to be in thermal equilibrium with temperature T , we can average the reaction probability with a Boltzmann distribution

$$P_{\text{react}}(\mathbf{i}, T) = \sum_{\mu} \exp\left(\frac{E_{\mu}}{kT}\right) P_{\text{react}}(\mathbf{i}, \mu) = \sum_{\mu} \int dQ \exp\left(\frac{E_{\mu}}{kT}\right) |\chi_{\mu}(Q)|^2 P_{\text{react}}^{\text{VSA}}(\mathbf{i}, Q)$$