



# Quantum mechanical theory diffusion in solids. An application to H in silicon and Li in LiFePO<sub>4</sub>



Donat J. Adams

*Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland*

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## ABSTRACT

We develop a fully quantum mechanical formalism to calculate ionic transition states in solids and determine diffusion constants for H in Si and Li and Fe in LiFePO<sub>4</sub>. The formalism is quantitative and does not involve empirical parameters.

From the quantum mechanical treatment we recover some quantities known from classical theory, e.g. the temperature dependent diffusion constant reflects the activation energy at high *T*. At low temperature however we discover a constant diffusion rate linked to the ionic tunneling. Tunneling and hopping rates are considered on an equal footing and result from the same formalism. We apply the quantum mechanical formalism to the diffusion of H in Si and discover the influence of the zero point energy of the diffusive species in the potential well. For LiFePO<sub>4</sub> we shed some light on the importance of the cross channel diffusion probably intermediated by Fe anti-site vacancies in the understanding of the experimentally observed diffusion constant. This work opens up the possibility to study quantitatively diffusion e.g. in potential electrode materials for Li-ion batteries.

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## 1. Introduction

Chemical energy storage by intercalation of ions will become increasingly important for future environmentally friendly society. Metal hydride tanks for fuel cells, Li-ion batteries etc. are spreading into large scale applications such as electric cars and mobile electronics already now. Therefore the knowledge about diffusion mechanism of ions in solids is of great interest.

Degradation and lifetime of intercalation materials are also strongly linked to ionic diffusion: The self-diffusion of metal ions [1] and the reconstruction in the cathode in absence of the intercalation species are suspected to cause up to 20% of the degradation [2]. Their relative importance compared to the better known degradation mechanism such as solid electrolyte interface (SEI) layer formation [3,4,5,6], decomposition of the organic electrolyte [7], mechanical stress [8,9] and disintegration are of large interest.

In order to face these questions a reliable and quantitative formalism is needed. It should also apply to the faster and better known diffusion mechanisms of H in silicon and Li in LiFePO<sub>4</sub>. Both have been discussed controversially in literature [10,11,12,13]. In this article we will focus on these systems in order to show the performance of the formalism developed further down. Leaving the investigation of the slower diffusion of metal ions for further investigation.

Diffusion is linked to the displacement of atoms due to thermal excitations and quantum effects such as quantum-tunneling. It is studied sometimes by Quantum Monte Carlo [14] or by Molecular Dynamics (MD) [15]. Both are computationally costly, rather inefficient and the extracted quantities suffer from sometimes large statistical uncertainties. In order to accelerate the hopping rate, temperatures of several thousand degrees are applied, which can hamper the interpretation of the results.

More targeted is the inspection of the potential energy surface of the solid as a function of ionic displacement in order to detect diffusion paths [12,16,17]. Decent results justify the application of semiclassical formalism transition state theory [18] in order to estimate diffusion rates. In particular it has been found, that in LiFePO<sub>4</sub> due to rapid hopping, delocalization of lithium ions and the coupling with polarons the harmonic approximation breaks down [10,19]. Therefore new computational approaches for the calculation of the diffusion rate including quantum mechanical effects are needed. Particularly in potential electrode materials, the potential energy profiles turn out to be sensitive on the partial charges on the ions [11], on the crystal phase [20] and concerted hopping increases the diffusion rate [21].

The limits of the semiclassical description are not clear. Furthermore it involves semi-empirical parameters such as the effective hopping frequency which shows the qualitative character of that theory.

Seeking to compute quantitative diffusion rates we introduce a quantum mechanical formulation in the first section of this article.[22] This is done on the basis of the determination of eigenstates of anharmonic potential wells [23], without recurrence to semiclassical

*E-mail address:* [donat.adams@empa.ch](mailto:donat.adams@empa.ch).

approximations [24]. The formalism will be tested through application to fast and well studied diffusion of H in Si, and Li in LiFePO<sub>4</sub>. Our aim is to address the capacity fade due self-diffusion of Fe in LiFePO<sub>4</sub> in a follow-up article.

## 2. Method

We sample transition states based on minimum energy pathways and saddle points connecting ionic binding sites. The potential energy surface is determined by e.g. nudged elastic band (NEB) calculations in Refs. [11,12].

Ions in the crystal lattice can be described by ionic Bloch states. For each point in reciprocal space  $k$  we calculate separately the eigenstates as a superposition  $\psi_{k,K}(x) = \sum_K c_{k-K} e^{iKx} \cdot b_K(x)$  of localized states  $b_K(x)$ .

As a basis we use trigonometric functions  $\cos(K \cdot x)$  and  $\sin(K \cdot x)$  with  $K = p \cdot \frac{2\pi}{a}$ , where  $a$  is the length of the well and  $p$  is an integer. The corresponding Schrödinger equation reads as

$$\left\langle \psi_{-k,K}(x) \left| -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right| \psi_{k,K}(x) \right\rangle + \left\langle \psi_{-k,K}(x) | V_k(x) | \psi_{k,K}(x) \right\rangle = \delta_{K,K'} \varepsilon(k). \quad (1)$$

When studying single particle diffusion we can replace  $V_k$  by  $V_0$ , which is given e.g. in Refs. 11 and 12. As a result we obtain the energy bands  $\varepsilon_j(k)$ , see e.g. Fig. 2. The bands appear flat allowing for further simplifications as we will show. We calculate the average velocity of a band

$$v_j = \frac{1}{\Omega} \int_{\text{BZ}} v_j(k) dk \quad (2)$$

Where  $\Omega$  is the volume of the first Brillouin zone and the velocity is derived through the dispersion of the bands

$$v_j(k) = \frac{1}{\hbar} \frac{d}{dk} \varepsilon_j(k). \quad (3)$$

Apart from the average band velocity (Eq. (2)), in what follows we will consider all quantities at  $k=0$ , which is justified by the flatness of the bands.

According to Vineyard (Ref. [25]) the transition rate  $\Gamma$  across the potential barrier can be determined through integration in configuration space

$$\Gamma = \frac{I}{Q_A} \quad (4)$$

where  $I$  is the number of states crossing the saddle point of the barrier, and  $Q_A$  the total number of accessible states in the system. We develop this expression for quantum mechanical states naturally as

$$\Gamma = \sum_j \frac{V_j}{a_0} \cdot g_j(T) \cdot \left| \psi_0 \left( \frac{a_0}{2} \right) \right|^2. \quad (5)$$

where  $g_j(T)$  is the occupation number of state  $j$  within the Bose–Einstein statistics

$$g_j(T) = \frac{1}{e^{\varepsilon_j - \mu} - 1}. \quad (6)$$

In Eq. (5) we have used the fact, that  $Q_A$  represents the total number of accessible states and is included in the occupation number  $g_j$ . It affects a renormalization. The number of states crossing the saddle point of the barrier is the product of the particle density  $|\psi_0(\frac{a_0}{2})|^2$ , the occupation

number and the frequency  $\frac{V_j}{a_0}$  at which they are accessed. Then the diffusion constant  $D$  expresses as

$$D = \Gamma \cdot (a_0)^2. \quad (7)$$

With this approach we go further than earlier works [26]. On the one hand we do not artificially constrain the ions between two sites, but calculate eigenstates. Furthermore we release the concept of the jump frequency [27], which is based on the classical view of the problem.

We apply this formalism to known potential wells from Ref. [12] for H diffusion in Si and Ref. [11] for Li diffusion in LiFePO<sub>4</sub>.

## 3. Results

### 3.1. H diffusion in Si

Based on the effective potential [12] of H<sup>+</sup> in silicon we calculate the eigenstates and diffusion-constants in order to compare them to other computational results as well as experimental ones in Fig. 3. From the slope of the diffusion we calculate an effective activation energy of 0.40 eV, somewhat below the potential height of 0.45 eV. This is due to a quantum mechanical correction – the zero point energy of the ion within the well – which is 0.036 eV: It reduces the energy to overcome during diffusion.

The diffusion coefficient is linear in the particle density (see further down for LiFePO<sub>4</sub>), i.e. for a reduced number of particles available for diffusion  $\log D$  is shifted vertically in the representation in Fig. 3, while as the slope [28] of  $\log D$  remains unchanged. The calculated slope of  $\log D$  coefficients fall between the TBMD data of Panzarini and Colombo [13], the TBMD data of Bédard and Lewis [29] and the *ab initio* MD calculations of Buda et al. [30]. The underlying potential energy maximum appears to be higher in the TBMD and smaller in *ab initio* MD which is reflected by their corresponding slope.

Due to the large spread of the experimental data (Refs. [31–37]) it is difficult to judge the quality of the different works. We just state, that the quality in the description of the atomic interaction appears to be transferred to the calculation of the diffusion constant  $D$ , independently of the method to calculate  $D$ . Consequently the atomic potentials used for the determination of  $D$  seem to play an important role.

Furthermore, we access the low temperature limit of the diffusion  $D_{T \rightarrow 0} = 5.15 \cdot 10^{-20}$  (see Fig. 3 inset). At about 100 K the population is mainly on the ground state. However, this state has some density at the maximum of the potential well, which is a requirement for the tunneling and thus tunneling can take place (see also Eq. (5)).

### 3.2. Li diffusion in LiFePO<sub>4</sub>

The formalism developed above is then applied to the diffusion of Li<sup>+</sup> in LiFePO<sub>4</sub> according the minimum energy paths determined elsewhere (Ref. [11]). We infer from other studies [10,15] that the geometric diffusion path is bended and therefore longer than the distance between two Li-sites. This can be taken into account by stretching the reaction coordinate given in Ref. [11] by a factor  $\sqrt{2}$ . However, the impact of the stretching on the eigen-energies is not significant.

Solving Eq. (1) we obtain energies and eigen-states of the Li-ion (and of the vacancies) within the respective potential well as shown in Fig. 2 (inset). We find that states with an odd number of nodes alternate with states with an even number of nodes. Furthermore the odd states appear to be more confined within the potential well and due to their symmetry show a zero crossing at the maximum of the potential well. They therefore cannot contribute to diffusion [42].

We then apply Eq. (7) to these states. In order to cover previous experimental and theoretical data, we create datasets with scaled barrier amplitudes ( $V_{\max}$ ) between 0.19 and 0.9 eV (blue lines in Fig. 4). We compare different potential shapes (Fig. 1 in Ref. [11]: profile for Li vs.

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