On the atomistic behavior of metal surfaces under high electric fields

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This work brings light on the dynamic behavior of metal surfaces under high electric fields on the atomic scale. Combining classical electrodynamics and density functional theory (DFT) calculations, we propose a general and rigorous theoretical framework where we show that the behavior of a surface atom in the presence of an electric field can be described by the polarization characteristics of the permanent and field-induced charges in its vicinity. We use DFT calculations for the case of a W adatom on a W{110} surface to confirm the predictions of our theory and quantify its system-specific parameters. Our quantitative predictions for the diffusion of W-on-W{110} under field are in good agreement with experimental measurements. This work is a crucial step towards developing atomistic computational models of such systems for long-term simulations.

The interaction of metal surfaces with an applied electric field is well understood within the continuum-limit classical electrodynamics [1]. However, how exactly this knowledge is translated to the sub-nanometer scale in order to predict, for instance, the behavior of surface single point defects under an electric field is not yet clear. Knowing the exact mechanisms driving the evolution of a metal surface under electric field is critical for developing modern nanotechnologies [2–5]. Furthermore, various existing and projected devices such as electron and ion sources [6–10], atom probe tomography [11–14], field ion and field emission microscopy [6, 15, 16], or even large-scale particle accelerators etc. [17–20] would significantly benefit from the existence of such a theory.

There are many indications in the literature that metal surfaces behave differently under the influence of a high electric field [2, 3, 21–28]. For example, the surface diffusion coefficient of adatoms was found to depend on the magnitude of the applied field [29–31]. Moreover, the field is known to modify the binding energy of an adatom, which plays a major role in the description of thermal and field evaporation [30, 32, 33]. In spite of the aforementioned significance and various experimental and theoretical studies since the 1960s, the theoretical understanding of such surface-field effects remains insufficient.

The behavior of adatoms on metal surfaces in the presence of an electric field has attracted interest of both theoretical and experimental studies since the 1970s [23, 30, 34–38]. For example, Tsong and Kellogg [23] attempted to describe it theoretically in terms of the polarization characteristics of the adatom on the surface. They proposed a formula describing the biased diffusion of such an adatom due to an electric field gradient. They assumed that the field effect on the diffusion of the adatom is determined solely by its own polarization characteristics. Although the latter is a crude approximation that neglects the significant charge redistribution in the vicinity of the adatom, this approach provided an intuitive phenomenological tool to describe the adatom behavior, in accordance with similar empirical formulae for the binding energy in the presence of an electric field suggested in refs [32, 34, 39].

In this letter, we develop a theory based on first principles that is able to explain the behavior of a metal surface under high electric field on the atomic level. We use our theory to predict and explain the observable behavior of adatoms on any metal surface under both uniform and non-uniform high electric fields. We also validate it by density functional theory (DFT) calculations of the W adatom migration barrier on the W{110} surface under electric fields. Finally, our theory establishes a general DFT methodology for calculating the electric field effects on the migration barriers on any metal surface configuration.

FIG. 1. Charge redistribution induced by (a) the presence of an adatom (no external field), (b) a positive 3 GV/m applied field (anode) on a system with adatom. The open surface of the W slab is of the {110} kind. Cyan and magenta colored areas correspond to increased and decreased electron densities, respectively, that are larger than a threshold value. The thresholds are 1% of the maximum electron density of the reference system in (a), and 0.1% in (b).

An applied electric field causes charge redistribution on metal surfaces by shifting the electron densities with respect to the position of positive surface nuclei either out from the surface or into the bulk, depending on the direction of the field. Similarly, the presence or the absence
of an atom, causes charge redistribution in its vicinity as well. Fig. 1 gives an illustration of how the charge distribution is modified in both cases. This illustration shows the actual electron density obtained by our DFT calculations for a W adatom on a perfect W(110) surface. It is clear that the effect of the presence of an adatom spreads well beyond its position, thus the whole charge density \( \rho(\vec{r}) \) in its vicinity has to be analyzed.

The interaction of a charge distributed as \( \rho(\vec{r}) \) in a system under a uniform electric field \( \vec{F} = \hat{z}F \) (we assume without loss of generality that the applied field is along \( z \)) changes the value of the total energy of the system. The field-induced component of the total energy can be obtained by analyzing the behavior of the corresponding total dipole moment \( \vec{p} = (p_x, p_y, p_z) = \int \rho \vec{r} dV \). An infinitesimal increment of the uniform field \( \delta \vec{F} \) applied to a system with a dipole moment \( \vec{p} \) induces an infinitesimal change of the total energy (see eq. (11.3) of ref [40])

\[
\delta E = -\vec{p} \cdot \delta \vec{F}.
\]

Therefore, if the relation \( \vec{p}(\vec{F}) \) is known, the energy of the system under the field can be found as

\[
E(\vec{F}) = E(0) - \int_0^{\vec{F}} p_z(F') dF' \tag{1}
\]

where \( E(0) \) is the total energy of the system in the absence of an external field. For small fields, the relation \( p_z(F) \) can be represented as a Taylor expansion

\[
p_z(F) = \mu + \alpha F + O(F^2) \tag{2}
\]

where \( \mu \) is the permanent dipole moment and \( \alpha \) is the polarizability of the system. Using eq. (2) in eq. (1) we obtain the total system energy

\[
E(\vec{F}) = E(0) - \mu \vec{F} - \frac{1}{2} \alpha \vec{F}^2 + O(\vec{F}^3). \tag{3}
\]

Equation (3) gives the basic relation between the applied field and the total energy of a system determined by only two parameters: the total permanent dipole moment and polarizability. The latter are specific for a given system configuration, but can be found, for instance, using DFT calculations. Knowing accurate values of these parameters will allow for a clear understanding of modifications on the activation energies of many processes, such as migration or evaporation, responsible for the evolution of metal surfaces under high electric fields.

Focusing our analysis on the migration and the evaporation of a surface atom, we consider a rectangular metal slab with a surface normal to the \( z \) axis. The total energy of such a system can be described in terms of its charge distribution according to eqs. (2) and (3). See the Supplementary Material sec. 1 (SM1) for a detailed analysis of the physical meaning of \( \mu \) and \( \alpha \) for such a system.

The migration energy barrier of an atom is the minimum work required for its transition to a new site. It is therefore defined as the difference in the total energy between two system configurations: one with the adatom at the saddle point (denoted by subscript \( s \)), where \( E \) assumes the highest value along the migration path, and the other at the initial lattice site (denoted by subscript \( l \)). Thus,

\[
E_m \equiv E_s - E_l = E_m(0) - \mu_{sl} \vec{F} - \frac{1}{2} \alpha_{sl} \vec{F}^2 \tag{4}
\]

where \( E_m(0) \) is the barrier without field, \( \mu_{sl} \equiv \mu_s - \mu_l \) and \( \alpha_{sl} \equiv \alpha_s - \alpha_l \).

The binding energy of an atom to a metal surface in our calculations is defined as the work needed to detach the atom from the surface. We find it as:

\[
E_b \equiv E_r + E_a - E_l = E_b(0) - \mu_{sl} \vec{F} - \frac{\alpha_x + \alpha_y - \alpha_l}{2} \vec{F}^2 \tag{5}
\]

where the subscript \( r \) denotes the reference system (substrate surface in the absence of the moving atom), \( a \) denotes the isolated neutral atom and we have assumed \( \mu_a = 0 \) due to the symmetry of the free atom. We note that a formula of the parabolic form (5) was proposed under semi-empirical considerations in refs [32, 34, 39]. Below we show that the parabolic form can be physically motivated in a rigorous manner and its coefficients numerically estimated with state-of-the-art ab-initio calculations.

Let us now consider the migration barrier in the presence of a small electric field gradient \( \gamma \equiv dF/dx \) along the migration direction \( x \). Such a gradient may appear due to surface features that locally distort the applied field. In this case, our fundamental equation (3) and the derived expressions (4) and (5) are not valid directly and the estimation of migration barriers becomes more complicated. Nevertheless, we show that when \( \gamma \) is sufficiently small, the barrier \( E_m \) can be asymptotically approximated by a formula similar to (4).

To this end, we shall write the total energy of the system \( E(\vec{r}_i) \), when the migrating atom lies at a surface point \( \vec{r}_i = (x_i, y_i, z_i) \), as

\[
E(\vec{r}_i) = E_r + \Delta E(\vec{r}_i) \tag{6}
\]

where \( \Delta E(\vec{r}_i) \) is the energy added to the system due to the introduction of the atom under study at \( \vec{r}_i \), \( E_r \), i.e. the reference system energy in the absence of the atom, is independent of the position \( \vec{r} \), therefore does not enter the expressions for the migration barrier, i.e.

\[
E_m = \Delta E(\vec{r}_s) - \Delta E(\vec{r}_l). \tag{7}
\]

\( \Delta E(\vec{r}_i) \) depends on interatomic interactions and interactions of charges with the external electric field that are localized around \( \vec{r}_i \). In other words, only the values of \( F(x) \) in the vicinity of \( x_i \) affect it. As one can see in fig. 1a, the charge redistribution due to the introduction of the atom is significant only within a certain cut-off radius \( R_c \), which in the simulated system does not exceed 1-2 lattice constants.

We now demand that the gradient of the field is sufficiently small so that \( \gamma R_c \ll F(x_i) \), i.e. the change of the field within \( R_c \) is negligible. If so, we can neglect any
changes of the field in the area surrounding the moving atom and assume that $F(x) \approx F(x_i)$, where $F(x_i)$ is the field at the exact position $r_i$. In this case, $\Delta E(r_i)$ can be approximated by its value under the corresponding uniform field $F(x_i)$. If we substitute the specific points $r_s$ and $r_l$ in eq. (7) and use (6) we obtain

$$E_m \approx (E_s(F_s) - E_r(F_s)) - (E_l(F_l) - E_r(F_l)) \quad (8)$$

with $E_i(F_i)$ being the total energy of the system in the configuration $i$ under a uniform field $F_i = F(x_i)$. Here $i$ stands for $s$, $l$ or $r$.

By combining eq. (8) with (3), we obtain our final formula for the barrier under a non-uniform electric field

$$E_m \approx E_m(0) - \mu_\text{sl} F_l - \frac{\alpha_\text{sl}}{2} F_l^2 - \mu_\text{sr} \Delta F - \alpha_\text{sr} F_l \Delta F \quad (9)$$

where $\Delta F \equiv F(x_s) - F(x_l) = \gamma(x_s - x_l)$. The first three terms of expression (9) are identical to eq. (4) and give the modification of the barrier in the presence of the electric field. The last two terms introduce the directional modifications due to the field gradient.

The unknown $\mu$ and $\alpha$ parameters in eqs. (4), (5) and (9) can be calculated for a specific system by using DFT, which allows the full quantum mechanical calculation of the total ground-state energy of a system in the presence of an electric field [41]. Furthermore, we can obtain the charge distribution in the entire system and calculate its total dipole moment by numerical integration. Finally, the barriers and the binding energies may be directly estimated by comparing the ground-state energies of different configurations.

![Graph showing total energy of four W systems simulated by DFT versus applied field.](image)

FIG. 2. Total energy of the four W systems simulated by DFT vs. vs the applied field. Black dots and green diamonds in (a) correspond to the system with an adatom at the saddle point and at the lattice site, respectively. Black dots in (b) and (c) correspond to the flat reference and isolated atom systems, respectively. The corresponding solid-line curves indicated by arrows are obtained by eq. (3) with parameters that are fitted to the same DFT data.

Here we calculated all the parameters for the example case of a single W adatom on a flat W[110] surface. For this purpose we ran DFT simulations for four different system configurations: the flat [110] surface ($r$), the surface with an adatom positioned at the saddle (bridge) point ($s$), with the adatom at the lattice (hollow) point ($l$) and an isolated W atom in vacuum ($a$). For our DFT calculations, we used VASP [42–49] with the Perdew-Burke-Ernzerhof [50] functional and various other established computational methods [51–54] that are explained in detail in SM2.

Fig. 2 shows the total energy of these systems versus the applied field as calculated by DFT (markers). We see that the DFT data follow a parabolic shape as predicted by eq. (3). Thus we can obtain $\mu$ and $\alpha$ for all systems by fitting them to the DFT data. The calculated values along with their error estimates can be found in SM3. As one can see in fig. 2 and table S1, the fitting results (solid lines) follow the DFT data fairly accurately with very small error margins.

As an additional confirmation that the fitted values of $\mu$ and $\alpha$ correspond to the actual permanent dipole moment and polarizability for all systems, we compared the total dipole moment $\mu$ (for this system due to symmetry $\mu = \bar{p} z$) as calculated by numerical integration of the charge density obtained with DFT and as predicted by the linear dependence of eq. (2) with the fitted $\mu$ and $\alpha$ values given in SM3. We obtained a perfect agreement, with an RMS error not exceeding 0.26% for any of the four systems. The small deviation is attributed to the numerical error in the integration of the electron density, which is discussed in detail in SM2.

In fig. 3, we plot the binding energy $E_b$ (green) and the migration barrier $E_m$ (black) versus a uniform applied field $F$. $E_b$ and $E_m$ were calculated according to eqs. (4) and (5), respectively. In order to validate these formulae, we also calculate these values directly from $E_s$, $E_l$ and $E_a$ as obtained by DFT. In the inset of fig. 3, we compare $E_m$ and $E_b$ as obtained by the formulae (solid lines) and by DFT (markers) for the range of fields (3 GV/m – 3 GV/m) where the used DFT method can produce meaningful results. The theoretical curves agree very well with the DFT data. We also note that the range of the fields used for the theoretical curves of fig. 3 is not accidental. It is dictated by the limits of validity of the assumptions used to develop the current model, which are discussed in detail in SM4.

On the anode side ($F > 0$), both $E_b$ and $E_m$ increase for small fields, because both linear terms $-\mu_\text{sl}$ and $-\mu_\text{sr}$ are positive, i.e. the permanent dipole in the lattice site is higher than both the saddle point and the flat system (the latter is 0). Then they reach a maximum around 10 GV/m where the negative quadratic terms start dominating and the inverse trend appears. On the other hand, both quantities are monotonously decreasing on the cathode side ($F < 0$). Therefore, any applied field would speed up the diffusion and promote evaporation on the cathode. On the contrary, the diffusion would slow down and the binding of the adatom with the W surface would become stronger for an anode field up to a certain turning point.

Considering the diffusion under a field gradient, which is described by equation (9), fig. 4 demonstrates both
the modifications of the barrier due to the applied field and the preferable direction of the biased diffusion due to the field gradient. Since we are here describing field differences, we plot the barrier versus the relative field increment \(dF = (F_s - F_l)/F_l\). Note that positive \(dF\) correspond to stronger fields for both the anode and the cathode. We see that the theoretical curves are in good agreement with the direct DFT values.

Again a different trend appears between anode and cathode, due to the linear \(\mu F\) term of eq. (9). On an anode, the diffusion is biased towards higher fields \((dF > 0)\) as has already been experimentally observed [23]. However, counter-intuitively, for small field gradients, the diffusion is preferable towards lower fields \((dF < 0)\) on a cathode. Nevertheless, the bias (indicated by the corresponding line slope) is much weaker than for the anode case and it weakens further as the applied cathode field increases. Above 11 GV/m fields, the cathode migration energy follows the same trend as for the anode, i.e. the diffusion is again biased towards stronger fields (see fig. 4). This turning point depends on the equilibrium between the fourth and fifth terms of equation (9).

The trends described above for both fig. 3 and 4 are determined by the balance between 1st and 2nd order terms of eqs. (4), (5) and (9). From a physical point of view, the 1st order terms correspond to \(\mu\)-values, i.e. the permanent dipole moment due to the adatom-induced charge redistribution, such as the one shown in fig. 1(a). On the other hand, 2nd order terms depend on how the field-induced charge redistribution (see fig. 1(b)) is modified in different configurations.

Furthermore, the \(\mu\) and \(\alpha\) coefficients of these terms might differ significantly for different migration processes and materials. Hence, our results for the simple W-on-W{110} are not enough to draw general conclusions on the diffusion on more complex surfaces. In order to do that, the \(\mu\) and \(\alpha\) parameters should be calculated for additional atomic migration processes. We leave this out of the scope of this work, which focuses on the theoretical framework upon which such calculations may be based.

We chose to perform DFT calculations for the W{110} system because experimental data of the diffusion on this specific system are available for comparison. Tsong and Kellogg (TK) [23] studied the biased diffusion of a single W adatom on a W{110} surface under an electric field with a gradient. If the barrier is considered to depend linearly on the field gradient as in eq. (9), a straightforward dependence of the coefficient of \(\Delta F\) to directly measurable quantities can be derived (see SM5 or ref [23]). From the measurements reported in ref [23], the coefficient was found to be 1.1 e\(\cdot\)A for an applied field \(F = 23.5\) GV/m. From our extracted values we obtain \(\mu_{ad} + \alpha_{ad} F = 0.88\pm0.03\) e\(\cdot\)A. This result is in a surprisingly good agreement with the experimental value; within an error of about 20%.

To conclude, this work provides a rigorous theoretical basis for understanding the atomistic behavior of metal surfaces under high electric fields and can be used to develop atomistic computational models for the long-term evolution of metal surfaces in this condition. We have showed that the behavior of a surface atom can be described with a few parameters in terms of the total dipole moment of both the permanent and field-induced charges in its vicinity. Our theory is in excellent agreement with DFT calculations and when we combine the two, we obtain results on the behavior of W adatoms on W{110} surfaces that are in very good agreement with experiments.
The $z$ component of the dipole moment which determines the energy can then be expressed as

$$p_z = \mu + A\epsilon_0\Delta z F \approx \mu + \alpha F$$  \hspace{1cm} (S6)$$

where $\Delta z = z^{(+)} - z^{(-)}$ is the vertical distance between the centers of mass of the charge layers and we can define $\alpha = \epsilon_0 A \Delta z$ as the total polarizability of the system.

From eq. (S5) it is evident that $\alpha$ scales linearly with the system volume and therefore cannot be considered a property of the surface or an atom. However, the differences in $\alpha$ such as $\alpha_{sl} \equiv \alpha_s - \alpha_t$ or $\alpha_{sr} \equiv \alpha_s - \alpha_r$, upon which characteristic transition energies depend, converge with the system size, i.e. are size-independent if the system is sufficiently large. This is because the differences in the charge distribution $\rho(\vec{r})$ due to a displacement of an atom are localized in its vicinity and therefore any point far from the atom would not contribute to the integral $\delta \vec{p} = \int (\delta \rho) \vec{r} dV$.

The physical meaning of $\alpha_{sl}$ and $\alpha_{sr}$ emerges from the above analysis. They are both proportional to the increase of the effective field-free volume of the metallic system due to the change on the surface. For a system with a given lateral area $A$, such as the one we simulated with DFT, differences in $\alpha$ are proportional to the corresponding shift of the charge layer due to the change on the surface.

Finally, we note that when defining $\alpha$ as $\epsilon_0 A \Delta z$ we assume that $\Delta z$ does not vary significantly with the applied field $F$. In case that this variation is taken into account, by expanding the function $\Delta z(F)$ as a Taylor series, $\alpha$ would be proportional to the zero order term of the expansion. Higher order terms would give $O(F^2)$ terms in eq. (S6), which are known as hyperrpolarizability terms. As shown by the DFT calculations presented in the main text, the $p - F$ curve is perfectly linear within the simulated range of field and small numerical error margins. However, when the fields approach the range of field evaporation, they might cause structural change of the surface in the vicinity of the atom under discussion and move the center of mass of the charge layer, thus introducing non-linearities. Then higher order terms might need to be taken into account.

**SM2. DFT calculations under electric field with VASP**

We simulated three slab systems for the W\{110\} surface: a slab with an adatom at the lattice (hollow) site, a slab with an adatom at the saddle (bridge) site and a flat slab with no adatom (reference system). These systems are illustrated in fig. S1(a-c) respectively. In the cases shown in (a) and (c), all ions were allowed to relax in all directions. In the saddle point case, an adatom was put in the middle of the bridge site; it was fixed in the $x$ and $y$ directions, while being allowed to relax along $z$. We used 8 monolayers of atoms in the $x$ direction, 10 in the $y$ and 7 monolayers in the $z$ (without counting the

**SUPPLEMENTARY MATERIAL**

**SM1. Physical meaning of the total polarizability $\alpha$**

In the main text the total dipole moment of a metal slab is expressed as

$$p_z(F) = \mu + \alpha F + O(F^2).$$  \hspace{1cm} (S1)$$

Here we shall analyze the physical meaning of the parameter $\alpha$ and its variation among different atomic configurations in terms of the field-induced charge layers.

Let us consider a rectangular metal slab, with its top and bottom surfaces perpendicular to the $z$ direction. If this system is introduced to the influence of a constant electric field $\vec{F} = F\hat{z}$, the free charge of the metal will redistribute in order to nullify the electric field in its interior. Thus two opposite charge layers at the top and the bottom of the slab will be formed.

The total charge per area in the top layer is

$$\sigma_+ = \frac{1}{A} \int_{\Omega_+} \rho dV$$  \hspace{1cm} (S2)$$

where $\Omega_+$ denotes the top half volume of the slab, $\rho$ is the local charge density and $A$ is the surface area of the $x - y$ plane of the slab. The corresponding bottom layer $\sigma_-$ can be defined equally for $\Omega_-$. By applying the Gauss law we obtain

$$\sigma_+ = -\sigma_- = F\epsilon_0$$  \hspace{1cm} (S3)$$

where $\epsilon_0$ is the dielectric permittivity of vacuum.

The center of mass of the charge layers can be defined as

$$\vec{r}_{cm}^{(i)} = \frac{\int_{\Omega_i} \rho \vec{r} dV}{\int_{\Omega_i} \rho dV}$$  \hspace{1cm} (S4)$$

where $i$ can be either (+) or (−). If we calculate now the total dipole moment of the system, we obtain

$$\vec{p} = \int_{\Omega} \rho \vec{r} dV = \vec{p}(F = 0) + A \left( \sigma_+ \vec{r}_{cm}^{(+)} - \sigma_- \vec{r}_{cm}^{(-)} \right).$$  \hspace{1cm} (S5)$$

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adatom as a layer) for the adatom simulations; we shall use the notation $8 \times 10 \times 7$ for these systems. A $2 \times 2 \times 7$ system was used for the calculations of the flat surface. This minimum system with the appropriate sampling of the Brillouin zone is mathematically equivalent to any $N \times N \times 7$, for the calculation of the ground-state energy. A 24 Å high vacuum was added on top of the slab for all systems. This vacuum height is measured from the highest fully populated atomic layer.

Additionally, we performed DFT calculations of a free W atom in vacuum with a large enough box so that the atom does not interact with itself over the periodic boundaries.

![Figure S1](image)

**FIG. S1.** Top view of the slab models for the W adatom: (a) a slab with the W adatom at the lattice site, (b) with the W adatom at the bridge (saddle), and (c) a flat surface.

All our DFT calculations were performed with the Vienna *ab initio* simulation package (VASP) and its corresponding ultrasoft-pseudopotential database [43–49]. VASP uses a plane wave representation for the wave functions. We used the Perdew-Burke-Ernzerhof [50] generalized gradient approximation (GGA) functional for all systems. This minimum system with the appropriate sampling of the Brillouin zone is mathematically equivalent to any $N \times N \times 7$, for the calculation of the ground-state energy. A 24 Å high vacuum was added on top of the slab for all systems. This vacuum height is measured from the highest fully populated atomic layer.

The electric field effect on the potential is implemented according to a scheme proposed by Neugebauer et al. in [41]. Within this scheme, an artificial dipole sheet is placed in the middle of the vacuum region that polarizes the periodic slab and introduces a uniform electric field on both sides of the slab. Our calculations were performed for electric fields up to 3 GV/m. Higher fields cannot be applied with this implementation, because electrons would tunnel towards the vacuum on the cathode side of the slab, thus causing a charge sloshing that disturbs the wave functions, the total dipole moment, and the total energy of the system [30].

A Gamma-centered k-grid was used in all the calculations: a $7 \times 7 \times 1$ grid for the systems with adatom and a $28 \times 28 \times 1$ k-grid for the $2 \times 2 \times 7$ flat slab. The cut-off energy of the plane wave basis was set to 600 eV. The above values were obtained after performing convergence tests, i.e. increasing the k-grid density and the cut-off energy until the total energy of the system converged. Our criterion for the convergence tests was 1 meV, therefore we will consider this value as our error margin for the ground-state energy calculations. This error margin is used to obtain the error bars of all direct DFT data plotted in the figures of the main text.

For each system under study, the permanent dipole moment $\mu$ and polarizability $\alpha$ were extracted from the ground state energy vs applied field curve ($E - F$), although it could also be done directly from the dipole moment vs applied field curve ($p - F$). The reason we chose the $E - F$ curve is that the calculation of $p$ from the DFT electron density has much larger numerical error than the corresponding calculations of energy values for a given computational effort [42]. This is due to the usage of a limited number of real-space mesh grid points in our calculations and the sensitive nature of the dipole moment integral (1st order moment of a spatially oscillating quantity). Furthermore, this effect produced an increased numerical error in the calculation of $p$ for the $2 \times 2 \times 7$ flat slab system due to its decreased number of real-space mesh points. Thus the corresponding $p - F$ curve gave a significant 5% deviation from the linear relation $p = \alpha F$. For this reason the dipole moment for the flat system was recalculated using a bigger system ($6 \times 8 \times 7$) for 5 field points in order to perform the comparison with the linear curve. The recalculated values of $p$ did give a very good agreement with the linear curve; the corresponding rms error was 0.1%.

### SM3. Values of the dipole characteristic parameters

Table S1 summarizes the fitted parameter values along with their corresponding error estimates. The error estimates noted as $\delta x$ for a quantity $x$ corresponds to the standard deviation of the obtained value. The latter is obtained from the corresponding element of the least square fit covariance matrix.

**Table S1. Permanent dipole and polarizability along with their error estimations (denoted with $\delta$) as obtained by fittings to DFT data for the four simulated systems.**

| quantity | lattice (l) | substrate (s) | free atom (a) |
|----------|-------------|---------------|---------------|
| $E(0)$ [eV] | -3522.707 | -3521.770 | -3510.910 | -3516.4048 |
| $\delta E(0)$ [eV] | $4 \times 10^{-5}$ | $4 \times 10^{-5}$ | $5 \times 10^{-4}$ | $5 \times 10^{-5}$ |
| $\mu$ [eÅ] | 0.3055 | 0.2735 | 0 | 0 |
| $\delta \mu$ [eÅ] | $10^{-4}$ | $10^{-4}$ | - | - |
| $\alpha$ [eÅ$^2$/V] | 27.740 | 27.771 | 27.51 | 0.659 |
| $\delta \alpha$ [eÅ$^2$/V] | $10^{-3}$ | $10^{-3}$ | $10^{-2}$ | $10^{-3}$ |

Table S2 summarizes the values of the parameters that determine the migration barrier and the binding energy, calculated according to the values of table S1. The error estimates noted as $\delta x$ for a quantity $x$ are calculated according to the error propagation rule applied to the
error margins given in table S1. We remind the reader that the notation \( x_{ab} \equiv x_a - x_b \) denotes the difference in the value of \( x \) between the system \( a \) and the system \( b \).

### SM4. Limitations of the theory

The considerations used to develop the current model limit the field region where it is valid for both the binding energy and the migration barrier. For \( F < -10 \text{ GV/m} \) (cathode fields higher than 10 GV/m), the field emission becomes significant and the space charge may affect the dynamics of the field distribution around the defect. Furthermore, due to the intense field emission initiating vacuum arcs, such fields are almost impossible to realize experimentally without causing an instant vacuum breakdown [21] and are therefore of limited interest. On the other hand, high positive fields also impose strict limitations due to the fundamental definitions of the migration barrier and the binding energy we use here.

The definition of the binding energy as \( E_b = E_r + E_a - E_l \) assumes that if one moves the adatom away from the surface under field, the total energy of the system will converge to \( E_r + E_a \) as the distance increases. However, at the fields approaching the field evaporation regime (30-60 GV/m for W) [11], the above assumption is not valid. In this case the applied field distorts significantly the potential "well" of the atoms, thus causing tunnelling of electrons from the atom towards the metal slab, even for high distances between the former and the latter. This means that the atom and the slab get partially charged, which adds a significant distance-dependent component on the total energy. Therefore the system energy decreases linearly with the atom-slab distance instead of converging, as we have assumed in our model. A detailed DFT calculation revealing this behavior for Al surfaces can be found in ref. [38].

To investigate the field regime where this behavior is expected to appear for W, we ran DFT simulations for an isolated W atom under high fields. Already at \( F = 10 \text{ GV/m} \) the system energy deviates significantly from the parabolic behavior shown in fig. 2c and the wave functions are non-zero in the vacuum region of the system. For this reason we limit the plot of the binding energy at below 10 GV/m.

The migration barrier, on the other hand, becomes rather meaningless when the activation energy for the field evaporation becomes comparably small or even smaller. This is because the atoms will see a potential "slide" towards the anode before they reach the new site. The evaporation activation energy has been measured to be 0.9 eV for a field of 47 GV/m [37]. According to our calculations, the migration barrier at this field is about 0.75 eV, which is close to the evaporation activation energy. Therefore, we limit our calculation for the barrier at fields up to 50 GV/m.

Finally, the limited range of the electric fields (\(|F| < 3–4 \text{ GV/m}\) in our calculations) that can be calculated by the current DFT technique [30] also affects the precision of the model at higher fields. Although the qualitative description of our theory can be considered valid up to 40–50 GV/m, the quantitative results might become inaccurate already at lower fields. This is because the error margins in the calculation of the polarization parameters \( \mu \) and \( \alpha \) are enough to give an significantly increasing uncertainty at high fields, as is evident from the increasing error bars of fig. 3. Furthermore, an additional uncertainty originates from the fact that second or higher order terms in eq. (2) might become significant at high fields and therefore equations (4), (5), and (9) need to be corrected with third and higher order terms as well.

### SM5. Comparison to the biased diffusion experiment

Tsong and Kellogg [23] conducted experiments of the biased diffusion of adatoms under a non-uniform field. They cut a W tip on its \{110\} surface and then placed an adatom on it. The position of the latter was monitored by field ion microscopy. Thus, they observed and measured the brownian motion of the adatom on the surface both in the presence and the absence of an applied field.

According to the brownian motion theory, when jumps in all directions are equally probable with an activation energy \( E_m \), the mean displacement after a time \( \tau \) is \( \langle x \rangle = 0 \) and the mean square displacement is

\[
\langle x^2 \rangle = \nu \tau l^2 \exp \left( -\frac{E_m}{kT} \right) \tag{S7}
\]

where \( \nu \) is the attempt frequency \( l \) is the length of the jump and \( kT \) is the temperature multiplied by the Boltzmann constant.

On the other hand, if the activation energy is \( E_m + \delta E_m \) on the left side and \( E_m - \delta E_m \) on the right, then the mean displacement of the biased diffusion is

\[
\langle x \rangle_b = 2 \nu \tau l \exp \left( -\frac{E_m}{kT} \right) \sinh \left( \frac{\delta E_m}{kT} \right). \tag{S8}
\]

The ratio between them is then

\[
\frac{\langle x \rangle_b}{\langle x^2 \rangle} = \frac{2}{l} \sinh \left( \frac{\delta E_m}{kT} \right). \tag{S9}
\]
If the bias is due to an applied field that has a gradient in a certain direction, as we assumed in our theory, we can substitute $\delta E_m$ by the function of the field and the field gradient given in eq. (9), i.e.

$$\delta E_m = (\mu_{sr} + \alpha_{sr} F) F = (\mu_{sr} + \alpha_{sr} F) \frac{l}{2}. \quad (S10)$$

Then the ratio becomes

$$\frac{\langle x \rangle_b}{\langle x^2 \rangle} = \frac{2}{l} \sinh \left( -l/\left( \frac{\mu_{sr} + \alpha_{sr} F}{2kT} \right) \right), \quad (S11)$$

which means that $\mu_{sr} + \alpha_{sr} F$ can be expressed as a function of directly measurable quantities, i.e.

$$\mu_{sr} + \alpha_{sr} F = \frac{2kT}{l\gamma} \sinh^{-1} \left( \frac{1}{2} \frac{\langle x \rangle_b}{\langle x^2 \rangle} \right). \quad (S12)$$

Now in ref. [23] both quantities were measured on the same surface under the same conditions. $\langle x^2 \rangle$ was measured without a field, whereas a field was applied to measure the biased displacement $\langle x \rangle_b$. By inserting the measurements in eq. (S12), Tsong and Kellogg obtained $\mu_{sr} + \alpha_{sr} F = 1.1 \text{ eÅ}$ for an applied field $F = 23.5 \text{ GV/m}$ and a field gradient $\gamma = 0.013 \text{ V/A}^2$. This value is very close to the value that we obtain from the values of tables S1 and S2 ($0.88 \pm 0.03 \text{ eÅ}$).

[1] J. D. Jackson, *Classical electrodynamics* (John Wiley & Sons, 2012).
[2] T. M. Mayer, J. E. Houston, G. E. Franklin, A. A. Erchak, and T. A. Michalske, *J. Appl. Phys.* 85, 8170 (1999).
[3] S. Fujita and H. Shimoyama, *Phys. Rev. B* 75, 235431 (2007).
[4] H. Yanagisawa, C. Hafner, P. Doná, M. Klöckner, D. Leuenberger, T. Greber, M. Hengsberger, and J. Osterverd, *Phys. Rev. Lett.* 103, 257603 (2009).
[5] H. Yanagisawa, V. Zadin, K. Kunze, C. Hafner, A. Aabloo, D. E. Kim, M. F. Kling, F. Djurabekova, J. Osterverd, and W. Wuensch, *APL Photonics* 1, 091305 (2016).
[6] R. Gomer, *Field emissions and field ionization* (American Inst. of Physics, 1992).
[7] K. Jensen, *Advances in Imaging and Electron Physics: Electron Emission Physics*, Vol. 149 (Elsevier, 2007).
[8] I. G. Brown, *The physics and technology of ion sources* (John Wiley & Sons, 2004).
[9] G. Harp, D. Saldin, and B. Tonner, *Phys. Rev. Lett.* 65, 1012 (1990).
[10] W.-C. Lai, C.-Y. Lin, W.-T. Chang, P.-C. Li, T.-Y. Fu, C.-S. Chang, T. Tsong, and I.-S. Hwang, *Nanotechnology* 28, 255301 (2017).
[11] M. K. Miller and R. G. Forbes, *Atom-probe tomography: the local electrode atom probe* (Springer, 2014).
[12] M. K. Miller, *Atom probe tomography: analysis at the atomic level* (Springer Science & Business Media, 2012).
[13] D. Perea, E. Hemesath, E. Schwalbach, J. Lensch-Falk, P. Voorhees, and L. Lauhon, *Nat. Nanotechnol.* 4, 315 (2009).
[14] T. Kelly and M. Miller, *Rev. Sci. Instrum.* 78, 031101 (2007).
[15] E. W. Müller and K. Bahadur, *Phys. Rev.* 102, 624 (1956).
[16] E. W. Müller, *Science* 149, 591 (1965).
[17] A. Descouedres, Y. Levinsen, S. Calatroni, M. Taborelli, and W. Wuensch, *Phys. Rev. Spec. Top. Acctl Beams* 12, 092001 (2009).
[18] C. Antoine, F. Peauger, and F. L. Pimpec, *Nucl. Instrum. Methods Phys. Res. B* 665, 54 (2011).
[19] M. J. Boland et al. (CLIC and CLICdp collaborations), *Updated baseline for a staged Compact Linear Collider*, Tech. Rep. CERN-2016-004 (Geneva, 2016).
[20] E. Z. Engelberg, Y. Ashkenazy, and M. Assaf, *Phys. Rev. Lett.* 120, 124801 (2018).
[21] W. Dyke, J. Trolan, E. Martin, and J. Barbour, *Phys. Rev. D* 91, 1043 (1995).
[22] W. Dyke and J. Trolan, *Phys. Rev. D* 89, 799 (1953).
[23] T. Tsong and G. Kellogg, *Phys. Rev. B* 12, 1343 (1975).
[24] S. Parvainen and F. Djurabekova, *Nucl. Instrum. Methods Phys. Res. B* 339, 63 (2014).
[25] S. Vigonski, F. Djurabekova, M. Veske, A. Aabloo, and V. Zadin, *Modell. Simul. Mater. Sci. Eng.* 23, 025009 (2015).
[26] M. Veske, S. Parvainen, V. Zadin, A. Aabloo, and F. Djurabekova, *J. Phys. D: Appl. Phys.* 49, 215301 (2016).
[27] A. Kyritsakis, M. Veske, K. Einire, V. Zadin, and F. Djurabekova, *J. Phys. D: Appl. Phys.* 51, 225203 (2018).
[28] F. Vurpillot, S. Parvainen, F. Djurabekova, D. Zanutini, and B. Gervais, *Mater. Charact.* (2018), 10.1016/j.matchar.2018.04.024, in press.
[29] G. Kellogg, *Phys. Rev. Lett.* 70, 1631 (1993).
[30] P. J. Feibelman, *Phys. Rev. B* 64, 125403 (2001).
[31] G. Antczak and G. Ehrlich, *Surface diffusion: metals, metal atoms, and clusters* (Cambridge University Press, 2010).
[32] R. G. Forbes and K. Chibane, *Surf. Sci.* 121, 275 (1982).
[33] R. G. Forbes, *Appl. Surf. Sci.* 87, 1 (1995).
[34] T. T. Tsong, *The J. Chem. Phys.* 54, 4205 (1971).
[35] T. T. Tsong and R. J. Walko, *Physica Status Solidi A* 12, 111 (1972).
[36] G. Kellogg, T. Tsong, and P. Cowan, *Surf. Sci.* 70, 485 (1978).
[37] G. Kellogg, *Phys. Rev. B* 29, 4304 (1984).
[38] C. Sánchez, A. Lozovoi, and A. Alavi, *Mol. Phys.* 102, 1045 (2004).
[39] M. Drechsler, V. Cosslett, and W. Nixon, in *Physikalisch-Technischer Teil* (Springer, 1960) pp. 13–
[40] L. Landau and E. Lifshitz, *Electrodynamics of continuous media*, 2nd ed. (Pergamon Press, 1984).
[41] J. Neugebauer and M. Scheffler, Phys. Rev. B **46**, 16067 (1992).
[42] G. Kresse, M. Marsman, and J. Furthmüller, VASP Group, Institut für Materialphysik, Universität Wien, Sensengasse.
[43] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[44] G. Kresse and J. Furthmüller, Computational Mater. Sci. **6**, 15 (1996).
[45] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[46] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[47] A. Pasquarello, K. Laasonen, R. Car, C. Lee, and D. Vanderbilt, Phys. Rev. Lett. **69**, 1982 (1992).
[48] K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, Phys. Rev. B **47**, 10142 (1993).
[49] G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).
[50] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[51] E. R. Davidson, in *NATO Advanced Study Institute, Series C*, Vol. 113 (1983) p. 95.
[52] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical recipes in C*, Vol. 2 (Cambridge university press Cambridge, 1996).
[53] M. Methfessel and A. Paxton, Phys. Rev. B **40**, 3616 (1989).
[54] G. Kerker, Phys. Rev. B **23**, 3082 (1981).