Instead of (2) we get the following new gradient system

$$\frac{dQ^i}{dt} = -m_i \frac{\partial U}{\partial Q^i}(Q^1/m_1^{1/2}, \ldots, Q^{3N}/m_{3N}^{1/2}) = -m_i \frac{\partial V}{\partial Q^i}, \tag{23}$$

$i = 1, \ldots, 3N$, for the former path of steepest descent. It is easy to see that (23) is identical to (2) because the following relationship is valid

$$\frac{d(Q^i/m_i^{1/2})}{dt} = -\frac{\partial U(Q^i/m_i^{1/2})}{\partial(Q^i/m_i^{1/2})}.$$

Consequently, the curves solving both systems will be the same in the configuration space of the real molecule if we start from the same initial point.

Our descent path is only related to the potential energy and does not depend on atomic masses, because the genuine potential itself is independent from these masses and depends per definition only on the charges and the mutual distances of the atoms and electrons [62, 63].

Contrarily to (2) or (23), Fukui et al. [49, 50] use the following system of ordinary differential equations

$$m_i \frac{dx^i}{dt} = -\frac{\partial U}{\partial x^i} \quad \text{or} \quad \frac{dQ^i}{dt} = -\frac{\partial V}{\partial Q^i}, \qquad i = 1, \ldots, 3N \tag{24a, b}$$

for pure Cartesian or mass weighted Cartesian coordinates respectively (see also [15–18, 22, 30, 31, 33]. It results a curve crossing the equipotential lines of the genuine potential in general not rectangularly, but in a skew angle (cf. Fig. 5 in [51]). Nevertheless, the solution curve is a descent path, which explains the success in the treatment of chemical model reactions. The use of (24) was claimed to be necessary for fixing the centre of mass of the chemical system instead of the geometrical centre. That means to replace (5a) by the requirements

$$\sum_{l=0}^{N-1} m_{a+3l} \frac{dx^{a+3l}(t)}{dt} = 0, \qquad a = 1, 2, 3 \tag{25}$$

additionally to Eq. (24a) [49]. Eq. (5b) will be changed similarly. For a simultaneous displacement of all nuclei we have

$$\sum_{l=0}^{N-1} \frac{\partial U}{\partial x^{a+3l}} = 0 \quad \text{(see Eq. 18).}$$

Thus we can satisfy Eq. (25) if we change the displacement of the steepest descent dx^i/dt of Eq. (2) by the mass-weighting of Eq. (24a). (Note that contrarily to the weighting in (24a) the so-called mass-weighted coordinates Q^i are only weighted by $m_i^{1/2}$. Eq. (24b) looks like a pure steepest descent path, if we take the mass-weighted potential for the genuine one by mistake. This is caused by the weighting of both the coordinates and the potential itself.)

The difference in the effect of Eqs. (2) and (24a) for the solution is evident in the simple case of two atoms. If r is greater than the equilibrium distance, $-\partial V/\partial r$ acts as a push on both nuclei to come closer. But there are different possibilities to displace two nuclei A and B: Firstly, the geometrical center can be held on $\frac{1}{2}(A+B)$, secondly, the center of masses can be conserved, or it is possible to fix any other particular "weighted" point between them. For example, A itself is fixed and only B moves towards A. We can realize this by cancelling three equations in (2) or in (23) for x^A, y^A, z^A. The same is available by the limes of a mass-weighting in (24) taking $m_A \to \infty$, $m_B = 1$ with the desired consequence $dx^A = dy^A = dz^A = 0$.

Now we can interpret our set of gradient equations as follows:

—Eqs. (2), (8), or (23) are the defining systems of ordinary differential equations for the invariant path of steepest descent on a genuine potential surface.

—Eq. (24) defines the ordinary differential equation for a *modified descent path* which preserves the centre of mass. It is in general not the path of steepest descent on the genuine potential. We can call it the mass weighted path.

Regarding the masses, the latter path is defined in a similar sense as it was done in trajectory calculations [33, 52] or in vibrational analysis [38, 54] but it cannot be interpreted as a trajectory (cf. also (vi)). The arbitrariness in this definition was already mentioned recently [55].

Omitting a sharp separation between the choice of coordinate systems and the question what the static descent path on a potential surface should mean physically, seems to be one source of misunderstanding in the literature. An example is given in Eq. (49) in [33]. This paper deals with mass-weighted coordinates, but in the equation pure Cartesians are used. The expression is similar to (24a). But there it is incorrectly remarked that this would be an opposite result in comparison to an equation of the (24b)-type.

(vi) A look to the dynamics. Mass-weighted coordinates are used for the calculation of vibrational frequencies [38, 54]. The crucial point is the assumption of a vibration across an equilibrium position. If we assume the vibrational equations to be approximately harmonic for small displacements, they are

$$m_i \ddot{x}^i + \sum_{j=1}^{3N} U_{ij} x^j = 0, \qquad i = 1, \ldots, 3N,$$

or

$$m_i^{1/2} \ddot{x}^i + \sum_{j=1}^{3N} \frac{U_{x^i x^j}}{(m_i m_j)^{1/2}} (m_j^{1/2} x^j) = 0,$$

hence

$$\ddot{Q}^i + \sum_{j=1}^{3N} V_{Q^i Q^j} Q^j = 0. \tag{26}$$

The weighting of the coordinates transfers the different kinetic action of the different mass points into the distorted curvature of V. From the analysis of the Hessian $V_{Q^i Q^j}$ the vibrational frequencies of a molecule can be deduced [38, 54].