Corrigendum of the paper 'On factorization of molecular wavefunctions' [J. Phys. A.: Math. Theor. **48**, 445201 (2015)]

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Abstract

We correct here a mistake in [1]. It turns out that it only slightly weakens the results of the paper.

The statement (21) in [1] is wrong. It was presented as a consequence of (20) but, since Ψ is a real analytic function of *several* variables, this logical link is false. Furthermore, (21) is actually false for some excited states of the hydrogen atom. Let us explain this in details. For the hydrogen atom, there is no nuclear variable R and the electronic variable r is the relative position of the nucleus and the electron. The collision set Σ is therefore the set of configurations for which $r = 0$. It turns out that some exited states do vanish on some sphere $\{r; |r| = \rho\}$ with positive radius ρ (see [2], p. 135). Thus such states have non isolated zeroes outside Σ.

The results in [1] does not concern the case of the hydrogen atom since they require the presence of a nuclear variable R. So it is important to check (21) in this situation. We do not know if (21) is valid.

Given a state Ψ, the statement (21) was (implicitly) used in [1] to show that the set $N_\Psi := \{R; \|\Psi(R;\cdot)\|_r = 0\}$ is included in Σ_n of nuclear collisions. We do not know if the last statement is true.

Now one can check that the results of the paper [1] remain valid provided one replaces "outside Σ_n" by "outside N_Ψ". In particular, the derivation from the factorisation of the non-linear system for the factors is justified *outside* N_Ψ. Conversely, if one starts with a solution $(\chi;\varphi)$ of the non-linear system then $\chi\varphi$ satisfies the molecular Schrödinger equation *outside* $Z_\chi \cup Z_{\|\varphi\|_r}$.

(Here Z_f denotes the set of zeroes of the function f.) If $Z_\chi \cup Z_{\|\varphi\|_r}$ has zero volume then $\chi\varphi$ is a molecular bound state.

We point out that, thanks to the analytic properties of Ψ, N_Ψ has zero volume and so does Z_χ, for χ given by (31) since $Z_\chi = N_\psi$. In particular, section VI remains valid after replacing "outside Σ_n" by "outside $Z_\chi \cup Z_{\|\varphi\|_r}$".

In the discussion in [1], one should again replace "outside Σ_n" by "outside N_Ψ". In particular, the use of the factorisation of Ψ is justified only "outside N_Ψ".

In [1], based on the wrong statement, we thought that the factorisation could be used at least outside the set of nuclear collisions, which does not depend on the molecular state under study. Now, we are not sure of this any more. Given a molecular state Ψ, the correction shows only that the factorisation can be used outside the unknown region N_Ψ.

References

[1] T. Jecko, B. T. Sutcliffe and R. G. Woolley, "On factorization of molecular wavefunctions", J. Phys. A.: Math. Theor. **48**, 445201 (2015).

[2] L. Pauling, and E. Bright Wilson, Jr., "Introduction to quantum mechanics with applications to Chemistry". Dover publications 1985.