Reply to "Dilatation analyticity and the radius of convergence of the $1/Z$ perturbation expansion: Comment on a conjecture by Stillinger"

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(Received 8 July 1976)

It is pointed out that Reinhardt's analysis assumes that wave-function normalizability persists up to the first real energy singularity. If this behavior is violated (as it is for the analogous square-well problem), then the analytically continued $E(\lambda)$ is neither prevented from crossing the first threshold, nor from exhibiting real singularities between thresholds.

Reinhardt's application of the theory of dilatation-analytic operators to $1/Z$ ($=\lambda$) perturbation theory provides some novel insights into the nature of atomic energy eigenvalues $E(\lambda)$. Reinhardt uses these insights to comment on our prior study of the analytic nature of $E(\lambda)$ for the two-electron problem.[1] In particular, he infers limitations on the possible singularities that $E(\lambda)$ might exhibit for positive real λ, and appears specifically to exclude the occurrence of a branch point between the first and second thresholds, $\lambda_1^{\rm crit}$ and $\lambda_2^{\rm crit}$.

If the wave function $\psi(\lambda)$ belonging to $E(\lambda)$ remains square integrable (this was implicitly assumed to be the case, without proof, in Ref. 1), then Reinhardt's conclusions must be accepted. However, another possibility exists which Reinhardt does not consider. $\psi(\lambda)$ might lose its square-integrability as λ passes $\lambda_1^{\rm crit}$, while at the same time $E(\lambda)$ remains analytic in λ. Then since $E(\lambda)$ for $\lambda > \lambda_1^{\rm crit}$ would no longer correspond to a normalizable eigenfunction, it is by definition no longer an eigenvalue. In short, the analytic continuation of an eigenvalue need not be an eigenvalue. Since Reinhardt's analysis was based strictly on theorems about eigenvalues, his conclusions do not apply to this latter possibility.

It might be worth noting that this situation, involving loss of wave-function normalizability, occurs for the ground state of the three-dimensional square well. As the interior potential $-V$ increases toward zero from large negative values, a well depth $-V^{\rm crit}$ is reached at which binding energy becomes zero. At this point the energy is in fact an analytic function of V, but the wave function transforms smoothly from exponentially decaying with distance (for $-V < -V^{\rm crit}$) to exponentially increasing (for $-V^{\rm crit} < -V$). Furthermore, the analytically continued energy function for this square-well example suffers a logarithmic branch-point singularity at $V=0$, which presumably one could deduce from an energy expansion in ΔV about some $V > V^{\rm crit}$. Significantly, $V=0$ is *not* a threshold value.

Of course the square well is not dilatation analytic. But no information available from Reinhardt's study or elsewhere currently can exclude analogous behavior in the atomic cases.

Under these circumstances, the two-electron ground-state energy function $E(\lambda)$ may indeed possess a branch point in $\lambda_1^{\rm crit} < \lambda < \lambda_2^{\rm crit}$, *provided* $\psi(\lambda)$ first loses normalizability. Power-series analyses for $E(\lambda)$, of the type advocated in Ref. 1, should be capable of detecting such singularities. Perhaps the results displayed in Ref. 1 require this modified interpretation.

Important alternatives also exist. The first is simply (as Reinhardt suggests), that $E(\lambda)$ is singular at $\lambda_1^{\rm crit}$. The second is that $E(\lambda)$ analytically continues past $\lambda_1^{\rm crit}$, to a higher threshold, but with its power-series convergence radius limited by singularities off the real axis. In this latter circumstance a very narrowly split pair of singularities spanning the real axis near the positive value λ^* would probably affect the low-order power-series coefficients (such as those used in Ref. 1) much as would one singularity at λ^* itself.

It seems obvious that more information is needed for full understanding of the analytic behavior of atomic perturbation problems. More than a decade has passed since publication of Midtdal's perturbation coefficients for the two-electron problem,[2] upon which the conclusions of Ref. 1 were based. It is timely and appropriate to turn present computing power to redetermination of the two-electron perturbation coefficients. This can surely be done to higher order than before, with scrupulous attention to convergence of individual coefficients with respect to basis-set size. The results could substantially sharpen our knowledge of the singularities of $E(\lambda)$.

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[1] F. H. Stillinger, J. Chem. Phys. 45, 3623 (1966).

[2] J. Midtdal, Phys. Rev. 138, A1010 (1965).