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LETTER TO THE EDITOR

The calculation of molecular resonances by complex scaling

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Abstract. We argue that the McCurdy–Rescigno and Moiseyev–Corcoran methods used to calculate molecular resonances can be viewed as finite-matrix approximations to the mathematically precise 'exterior complex scaling' method of Simon.

One of the more attractive pictures of atomic resonances is the method of complex scaling, reviewed extensively in Simon (1978). Briefly, the basic idea is to consider the action of the dilation operator $U(\theta)$ defined by

$$(U(\theta)\psi)(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n) = \exp(3n\theta/2)\psi(\mathrm{e}^{\theta}\boldsymbol{r}_1, \ldots, \mathrm{e}^{\theta}\boldsymbol{r}_n)$$

for appropriate ψ in $L^2(\mathrm{d}^3r_1 \ldots \mathrm{d}^3r_n)$, the space of square-integrable functions on $3n$-dimensional Euclidean space. For θ real $U(\theta)$ is readily seen to be unitary. It therefore follows that for θ real, $H(\theta) = U(\theta)H(U(\theta))^{-1}$ is unitarily equivalent to H, where H is a self-adjoint operator defined on a domain in L^2. Typically, H is a Schrödinger operator $T + V$, where T and V are the kinetic energy and the potential energy operators, respectively. One now considers the *non-Hermitian* operator $H(\theta) = U(\theta)H(U(\theta))^{-1}$, where $\operatorname{Im}\theta \neq 0$. If H is an atomic Hamiltonian, (i) the discrete energy levels of H remain as discrete energies of $H(\theta)$, (ii) the continuum rotates down about each atomic threshold by an angle $-2\operatorname{Im}\theta$ and (iii) as the continuum rotates down it uncovers complex eigenvalues, whose real and imaginary parts are associated with the position and the width, respectively, of atomic resonances.

On the one hand, there is a mathematically precise theory of complex scaling initiated by Aguilar and Combes (1971), Balslev and Combes (1971) and Simon (1972), which among other things leads to a proof of the convergence of time-dependent perturbation theory for autoionising resonances in atoms (Simon 1973). On the other hand, the method lends itself readily to finite-matrix approximations (variational calculations, but without a Rayleigh–Ritz principle) which have led to consistent results in agreement with experiments for few-electron systems; see Doolen *et al* (1978) for an especially impressive display of the numerical possibilities. Moreover, the method extends nicely to yield information about Stark resonances (Benassi *et al* 1979, Graffi and Grecchi 1978, Herbst 1979, Herbst and Simon 1978, Reinhardt 1976).

From a strictly mathematical point of view, one gap in the theory is that there are no precise theorems assuring the convergence of eigenvalues of the finite-matrix approximations to the eigenvalues of the non-self adjoint operators, $H(\theta)$, whose complex

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eigenvalues are the resonance energies. We raise this point because this gap prevents our arguments below from being rigorous theorems. We emphasise that in the atomic case, there is extensive numerical evidence for rapid convergence of the matrix approximations (see e.g. Doolen 1978) although in the Stark problem some apparent resonances have disappeared under passage to larger matrices.

This note concerns the extension of the method to molecular resonances, a subject on which there has recently been considerable discussion (McCurdy 1980, McCurdy and Rescigno 1978, Moiseyev and Corcoran 1979, Simon 1979). For a variety of reasons (see especially McCurdy and Rescigno 1978 and also Simon 1979) one wants to obtain resonance curves in a fixed nucleus (Born–Oppenheimer) approximation as functions of nuclear positions; that is, one only wants to scale electron coordinates and not nuclear coordinates. Unfortunately, for $\boldsymbol{R}$ fixed, $V(\boldsymbol{r}) = |\boldsymbol{r} - \boldsymbol{R}|^{-1}$ is not dilation analytic; the singularity at $\boldsymbol{r} = \boldsymbol{R}$ blossoms into a circle of square-root branch points in $V(e^{\theta}\boldsymbol{r})$ for θ non-real; see Simon (1978). This difficulty can also be seen by doing the complex scaling in momentum space. If $V(\boldsymbol{r}) = |\boldsymbol{r}|^{-1}$, $\hat{V}(\boldsymbol{p}) = 4\pi|\boldsymbol{p}|^{-2}$. Thus if $V_{\boldsymbol{R}}(\boldsymbol{r}) = |\boldsymbol{r} - \boldsymbol{R}|^{-1}$, $\hat{V}_{\boldsymbol{R}}(\boldsymbol{p}) = \exp(-i\boldsymbol{p} \cdot \boldsymbol{R})\, 4\pi|\boldsymbol{p}|^{-2}$. In momentum space $\hat{V}_{\boldsymbol{R}}$ acts as

$$\widehat{V_{\boldsymbol{R}}\psi}(\boldsymbol{p}) = 4\pi \int d^3\boldsymbol{q}\, \frac{\exp[-i(\boldsymbol{p}-\boldsymbol{q}) \cdot \boldsymbol{R}]}{|\boldsymbol{p}-\boldsymbol{q}|^2}\, \hat{\psi}(\boldsymbol{q}).$$

If $\boldsymbol{q}$ is replaced with $e^{i\theta}\boldsymbol{q}$, where $0 < \theta < \pi$, the kernel of the integral operator has exponential growth at infinity, with the result that $V_{\boldsymbol{R}}(e^{i\theta}\boldsymbol{r})\psi(e^{i\theta}\boldsymbol{r})$ is not even defined for a reasonable ψ such as the 1s eigenfunction of the hydrogen atom, where

$$\hat{\psi}(e^{-i\theta}\boldsymbol{p}) \sim (1 + e^{-2i\theta}|\boldsymbol{p}|^2)^{-2}.$$

Two seemingly distinct approaches have been proposed to overcome these difficulties. An approach dubbed 'exterior complex scaling' has been presented by Simon (1979, 1981) which only scales the electron coordinates outside some large sphere. This method is mathematically precise and has most of the nice mathematical properties of ordinary complex scaling, but it seems to be difficult to implement in calculations. Two related *ad hoc* methods of calculation have been proposed by McCurdy (1980), McCurdy and Rescigno (1978) and Moiseyev and Corcoran (1979). To oversimplify the proposals, we can describe them as explicit realisations of an *ad hoc* procedure suggested earlier by Yaris *et al* (1978). If the usual complex scaling theory works and if ψ is a dilation analytic vector, then

$$(\bar{\psi}, H(\theta)\psi) = (\overline{\psi(-\theta)}, H\psi(-\theta)) \tag{1}$$

where $\psi(\theta) = U(\theta)\psi$ and $H(\theta) = U(\theta)H(U(\theta))^{-1}$. The proposal is then to use the right-hand side of equation (1) to obtain finite-matrix approximations to a non-existent '$H(\theta)$' in cases where $H(\theta)$ is not meaningful. Of course, in general this can be a dangerous procedure: for example using inverse scattering methods, one can construct potentials for which the scattering amplitude will have a natural boundary as the real axis is approached. However, the above method will 'predict' resonance energies in such a situation where there is no second sheet.

One point of the exterior scaling theory is to guarantee the existence of a second sheet at least for matrix elements of the resolvent between dilation analytic vectors. Our purpose here is to explain why the eigenvalues of the McCurdy–Rescigno and Moiseyev–Corcoran methods can be viewed as finite-matrix approximations to the

positions of these second sheet poles. It is our hope that this realisation of a firm mathematical foundation will encourage further calculations with these methods.

For each $\varepsilon > 0$, let g_ε be the three-dimensional Gaussian

$$g_\varepsilon(\boldsymbol{r}) = (2\pi\varepsilon)^{-3/2} \exp(-|\boldsymbol{r}|^2/2\varepsilon) \tag{2}$$

which as $\varepsilon \downarrow 0$ approximates a δ function. Let

$$V^{(\varepsilon)}(\boldsymbol{r}) = \int g_\varepsilon(\boldsymbol{x}) |\boldsymbol{r} - \boldsymbol{x}|^{-1} \, \mathrm{d}^3 x. \tag{3}$$

This convolution technique is known as the Weierstrass transform and has been studied extensively (Hirschmann and Widder 1955). In general, the Weierstrass transform maps functions $f(\boldsymbol{x})$ with $\int \mathrm{d}\boldsymbol{x} f(\boldsymbol{x}) \exp(-\alpha|\boldsymbol{x}|^2) < \infty$ to analytic functions. Thus, for each $\varepsilon > 0$, $V^{(\varepsilon)}(\boldsymbol{r})$ is an entire function of $\boldsymbol{r}$; explicitly,

$$V^{(\varepsilon)}(\boldsymbol{r}) = \frac{1}{|\boldsymbol{r}|} \operatorname{erf}(|\boldsymbol{r}|/\sqrt{2\varepsilon})$$

where $\operatorname{erf}(z)$ is the error function, defined by

$$\operatorname{erf}(z) = 2\pi^{-1/2} \int_0^z \mathrm{d}t \exp(-t^2).$$

The smoothing effect of the Weierstrass transform is easily seen in momentum space: the singular kernel with exponential growth at infinity

$$4\pi \exp[-\mathrm{i}(\boldsymbol{p} - \mathrm{e}^{-\mathrm{i}\theta}\boldsymbol{q}) \cdot \boldsymbol{R}]/|\boldsymbol{p} - \mathrm{e}^{-\mathrm{i}\theta}\boldsymbol{q}|^2$$

is replaced by

$$\frac{4\pi \exp[-\mathrm{i}(\boldsymbol{p} - \mathrm{e}^{-\mathrm{i}\theta}\boldsymbol{q}) \cdot \boldsymbol{R}]}{|\boldsymbol{p} - \mathrm{e}^{-\mathrm{i}\theta}\boldsymbol{q}|^2} \left(\frac{2}{\pi}\right)^{3/2} \exp(-2\varepsilon|\boldsymbol{p} - \mathrm{e}^{-\mathrm{i}\theta}\boldsymbol{q}|^2)$$

which for $0 < |\operatorname{Im}\theta| < \pi/4$ has exponential fall off as $\boldsymbol{q}$ becomes large. Now fix some nuclear positions, $\boldsymbol{R}_1, \ldots, \boldsymbol{R}_k$ and let $H^{(\varepsilon)}$ denote the electron Hamiltonian for these nuclear positions with all Coulomb potentials $|\boldsymbol{x} - \boldsymbol{y}|^{-1}$ replaced by $V^{(\varepsilon)}(\boldsymbol{x} - \boldsymbol{y})$. For $R_0 > \max_j |\boldsymbol{R}_j|$, one can consider the exterior scaled Hamiltonian $H^{(\varepsilon)}_{R_0}(\theta)$ described in Simon (1979, 1981). For $|\operatorname{Im}\theta| < \frac{1}{4}\pi$, the potentials $V^{(\varepsilon)}_{R_0}(\theta)$ of equation (8) of Simon (1979) converge as $\varepsilon \downarrow 0$ uniformly to the Coulomb potential, so it is easy to prove that

$$\|(H^{(\varepsilon)}_{R_0}(\theta) - z)^{-1} - (H_{R_0}(\theta) - z)^{-1}\| \to 0$$

as $\varepsilon \downarrow 0$. Thus, by general principles (Kato 1976, Reed and Simon 1978) eigenvalues $E^{(\varepsilon)}$ of $H^{(\varepsilon)}_{R_0}(\theta)$ converge to eigenvalues E of $H_{R_0}(\theta)$.

Now consider finite-matrix approximations to all these problems using the right-hand side of equation (1). For $N \times N$ approximations, let E_N and $E^{(\varepsilon)}_N$ denote the corresponding eigenvalues. Clearly, by the above mentioned convergence of potentials, the right-hand sides of equation (1) converge so that for any finite N:

$$E^{(\varepsilon)}_N \to E_N \quad \text{as} \quad \varepsilon \downarrow 0.$$

The point is that since $V^{(\varepsilon)}$ is entire and has fall-off in the region $|\arg r| < \frac{1}{4}\pi$, the usual complex scaling theory applies to the Hamiltonians $H^{(\varepsilon)}$. Moreover, by the universality theorem of Simon (1979) the eigenvalues, $E^{(\varepsilon)}$ of $H^{(\varepsilon)}_{R_0}(\theta)$ are identical to those of the usual complex scaled Hamiltonian $H^{(\varepsilon)}(\theta)$. Therefore, to the extent that

one accepts finite-matrix approximations of dilation analytic problems, one should *assume* that

$$E_N^{(\varepsilon)} \to E^{(\varepsilon)} \quad \text{as} \quad N \to \infty.$$

If we make the further reasonable leap of faith that this last convergence is *uniform* in ε, then one has that

$$E_N \to E$$

i.e. the complex eigenvalues of the McCurdy–Rescigno and Moiseyev–Corcoran methods should converge to the resonances defined by exterior complex scaling.

To summarise; we view the methods of McCurdy (1980), McCurdy and Rescigno (1978) and Moiseyev and Corcoran (1979) as clever finite-matrix approximations to the precise mathematical theory of Simon (1979), and this view is supported by the apparent stability as N is increased in the calculations in McCurdy (1980), McCurdy and Rescigno (1978) and Moiseyev and Corcoran (1979). It seems to us that this type of finite-matrix approximation is about as firmly based as the kind of approximation used in ordinary complex scaling in atomic systems.

Thus far we have discussed only electron–molecule resonances. The same Weierstrass transform technique works also for resonances of molecules in an external constant electric field. This fact is quite trivial, for the convolution of any linear function with the three-dimensional Gaussian (equation (2)) is precisely the same linear function.

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Notes added in proof. After this article was submitted we saw two papers (Deguchi K and Nishikawa K 1980 *J. Phys. B: At. Mol. Phys.* **13** L511–4, L515–8), which relate the Gaussian convolution technique to the generator coordinate method (Lathouwers L, van Leuven P and Bouten M 1977 *Chem. Phys. Lett.* **52** 439).

R Junker (1981 *Phys. Rev. Lett.* to appear) has proposed a different way, exploiting the variational principle, of making the connection between exterior complex scaling and the calculation methods of McCurdy, Rescigno, Moiseyev and Corcoran.

References

Aguilar S and Combes J M 1971 *Commun. Math. Phys.* **22** 265
Balslev E and Combes J M 1971 *Commun. Math. Phys.* **22** 280
Benassi L, Grecchi V, Harrell E and Simon B 1979 *Phys. Rev. Lett.* **42** 704
Doolen G 1978 *Int. J. Quantum Chem. (Proc. 1977 Sanibel Workshop on Complex Scaling)* **14** 523
Doolen G, Nutall J and Wherry C S 1978 *Phys. Rev. Lett.* **40** 818
Graffi S and Grecchi V 1978 *Commun. Math. Phys.* **62** 83
Herbst I 1979 *Commun. Math. Phys.* **64** 279
Herbst I and Simon B 1978 *Phys. Rev. Lett.* **41** 67
Hirschmann I and Widder D 1955 *The Convolution Transform* (Princeton: Princeton University Press) ch 8
Kato T 1976 *Perturbation Theory for Linear Operators* (Berlin: Springer)
McCurdy C W 1980 *Phys. Rev.* A **21** 464
McCurdy C W and Rescigno T N 1978 *Phys. Rev. Lett.* **41** 1364
Moiseyev N and Corcoran C 1979 *Phys. Rev.* A **20** 814
Reed M and Simon B 1978 *Methods of Modern Mathematical Physics: Analysis of Operators* vol 4 (New York: Academic)
Reinhardt W 1976 *Int. J. Quantum Chem.* **10** 359

Simon B 1972 *Commun. Math. Phys.* **27** 1
—— 1973 *Ann. Math.* **97** 247
—— 1978 *Int. J. Quantum Chem.* (*Proc. 1977 Sanibel Workshop on Complex Scaling*) **14** 529
—— 1979 *Phys. Lett.* **71A** 211
—— 1981 to be submitted
Yaris R, Bendler J, Lovett R, Bender C and Fedders P 1978 *Phys. Rev.* A **18** 1816