THE DEFINITION OF MOLECULAR RESONANCE CURVES
BY THE METHOD OF EXTERIOR COMPLEX SCALING ☆

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We introduce an extension of complex scaling which is applicable to molecules in the Born–Oppenheimer approximation and which reduces to the usual complex scaling when that theory is applicable.

The method of complex scaling has become a standard tool in the understanding of atomic resonances. The theory is closely related to the notion of Gamow–Siegert [1] boundary conditions, i.e. of looking for solutions of the Schrödinger equation with exponential falloff in some complex direction. Versions of the theory on the level of ordinary differential equations [2] and deformations of integrals [3] were byproducts of the development of Regge theory. A version of the theory which is regarded as the definitive one follows a suggestion of Combes [4] that one deal with analytic continuation on the operator level of hamiltonians moved under the real scaling

$$U(\theta)\,\psi(r_1, ..., r_n) = e^{3N\theta/2}\,\psi(e^\theta r_1, ..., e^\theta r_n)\,. \qquad (1)$$

This suggestion was implemented by Aguilar, Balslev and Combes [5] with further development by others [6–8]. The scope of application runs the gamut from subtle mathematical questions like the absence of singular continuous spectrum [5], and the convergence of time-dependent perturbation theory [8], through detailed theoretical features of resonances in Coulomb fields, such as the absence of resonances at energies sufficient for total breakup [7–12] [1,2] and the resolution of the Stillinger problem [13] and finally to the detailed calculation of resonance positions in few-electron atoms [14].

In this context, it is of obvious interest to be able to apply the theory to the study of molecular resonances. At first glance, there appears to be no problem here since Coulomb potentials are dilation analytic so that one can scale all the coordinates, both electron *and nuclear* and get a system to which the Balslev–Combes theory applies. However, as emphasized by McCurdy and Resigno [15] [3], there are problems with this view: (i) Because of rotational and vibrational excitations, there are so many thresholds in the full problem that even if one could do the full calculation, in some finite basis, it would be difficult to determine which eigenvalues were associated to a cut and which to true resonances and which resonances were relevant in some particular physical process [4]. (ii) The necessity to scale the nuclear variables prevents one from working in a Born–Oppenheimer (BO) approximation. This means that one has a much more complex problem both from the point of view of calculation and in-

[1] It should be noted that there is one experiment (of Peart and Dolder [9]) which violates the general theorem, see ref. [10]. Since the general theorem depends on no approximation (other than that of taking a hamiltonian with purely coulombic potentials, i.e. dropping relativistic corrections) and since the energy is too large for the "resonance" seen to be some kind of threshold effect pretending to be a resonance, it seems imperative that the experiment be checked.

[2] Ref. [11] sketches a very elementary proof of Hunziker [12] of the no-resonance result.

[3] This paper in preprint form stimulated the research described here.

[4] This argument was given to me by W. Reinhardt.

terpretation then in the BO approximation. (iii) Most significantly [15], there should be BO resonance curves which do not correspond to resonances of the full system: after all, even on the level of bound states, there will be BO electronic curves which are repulsive — these will not correspond to bound states of the full system but are very useful for the understanding of certain processes.

We thus see that it is important to be able to discuss resonances for several electrons moving in the Coulomb field of several *fixed* nuclei and here the crunch comes since the resulting potential,

$$V(r) = \sum_{i=1}^{k} z_i |r - r_i|^{-1},\qquad (2)$$

is *not* dilation analytic about any center [11]. This can be seen by noting that $(e^{i\phi} r - r_0)^2 = 0$ $(r = (x, y, z)$ and $r_0 = (0, 0, r_0)$ real) corresponds to

$$z = r_0 \cos\phi,\quad x^2 + y^2 = (r_0 \sin\phi)^2,\qquad (3)$$

so, under scaling the singularity at r_0 turns into a circle of square root branch points! One might thus give up on applying complex scaling to this situation but our experience with complex scaling and the Stark problem [+5] should convince us of the flexibility of the method and lead us to find some modified approach which is applicable to this situation.

We wish to describe such an approach here; some of the more technical aspects of the problem will be described in a longer paper [18]. The method is motivated in part by consideration of the Gamow—Siegert boundary condition [1]; also, it clearly has some overlap with R-matrix ideas. For obvious reasons, we suggest calling the method "exterior complex scaling".

Consider first a one-dimensional problem on a half-line with a potential $V(x)$ which is not necessarily analytic in $(0, R_0)$ but which is analytic in $\{z | \text{Re } z > R_0\}$. The Gamow—Siegert method suggests we look for solutions which falloff exponentially along a curve $x \rightarrow R(x)$ $(\theta = i\phi, \phi$ real) with [+6]

[+5] As in the present case, the extension of the theory to a situation not covered by the Balslev—Combes paper was motivated by calculational work, especially by Reinhardt [16]. The mathematical theory can be found in ref. [17].

[+6] There is nothing sacred about this curve from the Gamow—Siegert point of view. However, it has the important property that when θ and θ' are real, $R(R(r, \theta), \theta') = R(r, \theta + \theta')$, which will yield the group property for our unitaries $U_{R_0}(\theta)$ defined below.

$$R(x) = x,\qquad\qquad 0 < x \leqslant R_0,\qquad (4a)$$

$$= R_0 + e^{\theta}(x - R_0),\qquad R_0 \leqslant x.\qquad (4b)$$

The boundary conditions for matching that one would try in this case are clearly (for $\psi(R(x))$)

$$\psi(R_0 - 0) = \psi(R_0 + 0),$$

$$\psi'(R_0 - 0) = e^{-\theta} \psi'(R_0 + 0).\qquad (5)$$

Motivated by this we introduce an operator on wave functions ψ of n three vectors $r_i = r_i \hat{\omega}_i$ with $r_i \in (0, \infty)$, $|\hat{\omega}_i| = 1$ by:

$$(U_{R_0}(\theta)\,\psi)(r_1, \hat{\omega}_1, ..., r_n, \hat{\omega}_n)$$

$$= J(r_1) \cdots J(r_n)\,\psi(R(r_1), \hat{\omega}_1, ..., R(r_n), \hat{\omega}_n),\qquad (6)$$

where $J(r_i)$ is (the square root of the jacobian):

$$J(r) = [R(r)/r]\,[dR/dr]^{1/2},$$

necessary for U to be unitary when θ is real and R is given by eq. (4) with θ real.

Since U_{R_0} is a one-parameter group it will have vectors analytic in θ say in the region $|\text{Im }\theta| < \pi/4$. In fact [18], when $n = 1$, any vector dilation analytic in the usual sense (i.e. for $R_0 = 0$) is analytic for U_{R_0} in this strip: this can be seen, for example, by making partial-wave expansions and reducing the result to the fact that a function analytic in $|\text{Arg } z| \leqslant \phi$ and L^2 for $|\text{Arg } z| \leqslant \phi$ is also L^2 for $|\text{Arg}(z - R_0)| \leqslant \phi$. For n electrons the situation is more complicated [18] but the critical fact is that there is a set $\mathcal{U}$ of vectors analytic for U_{R_0} which is dense in these vectors in the norms $\|U_{R_0}(i\phi) \cdot \|$, $|\phi| < \pi/4$ with $\mathcal{U}$ universal in the sense that it is independent of R_0. For example [18], one can let $\mathcal{U}$ consist of vectors η so that $\exp(\delta \Sigma r_i^2)\eta$ is dilation analytic in the usual sense *in each electron coordinate separately* and has

$$\exp\left(\delta \sum r_i^2\right)\eta \in D\left(\prod_{i=1}^{n}(1 - \Delta_i)^{1/2}\right);$$

δ runs through all strictly positive reals.

Let $H^{(0)} = -\Sigma \Delta_i$ and

$$H_{R_0}^{(0)}(\theta) = U_{R_0}(\theta)\,H_0\,U_{R_0}(\theta)^{-1}.$$

This operator is analytic for $|\text{Im }\theta| < \pi/2$ in the sense that it has an analytic resolvent [18]; it is not analytic

of type (A) but rather of type (B) [19] – that is, the operator domain is not invariant essentially since, after passing to partial waves, it involves both boundary conditions in eq. (5) but its form domain is invariant since that only involves the first boundary condition which is θ independent. Moreover

$$\sigma(H_{R_0}^{(0)}(\theta)) = e^{-2\theta}[0, \infty), \tag{7}$$

which might be surprising at first blush, can be proven as follows: the essential ($\equiv$ continuous) spectrum of $H_{R_0}^{(0)}$ comes from states that live near infinity [+7] where $J \sim e^{3\theta/2}$ and the particle is unaware of the special nature of a tiny region near zero. Thus

$$\sigma_{ess}(H_{R_0}^{(0)}(\theta)) = \sigma_{ess}(H_0^{(0)}(\theta)) = e^{-2\theta}[0, \infty).$$

There can be no eigenvalues since solutions of the equation $H_{R_0}^{(0)}(\theta)\psi = E\psi$ regular near $r_i = 0$ are sums of products of Bessel functions times spherical harmonics and so not square integrable.

One can now mimic the usual theory [5] and in particular consider

$$H_{R_0}(\theta) = H_{R_0}^{(0)}(\theta)$$

$$+ \sum_{j=1}^{n} V_{R_0}(\theta)(r_i) + \sum_{i<j} W_{R_0}(\theta)(r_i, r_j). \tag{8}$$

For molecular resonance theory, the main results [18] are the following:

(i) If V is local, central and dilation analytic in the usual form sense [7] under scaling centered at *some* point r_i with $|r_i| < R_0$, then V is $U_{R_0}(\theta)$ analytic. In particular, the V of eq. (2) is U_{R_0} analytic. Moreover, since $((R(r_1), \hat{\omega}_1) - (R(r_2), \hat{\omega}_2))^2 = 0$ implies that $\hat{\omega}_1 = \hat{\omega}_2, r_1 = r_2$, the Coulomb repulsion $(r_1 - r_2)^{-1}$ is $U_{R_0}(\theta)$ analytic. Thus eq. (8) makes sense for (BO) hamiltonians. One defines resonance, etc. in the usual way.

(ii) $\sigma_{ess}(H_{R_0}(\theta))$ consists of $(E + \lambda e^{-2\theta}, \lambda \geq 0,$ $E \in \Sigma)$ where [+8] Σ is the set of possible eigenvalues for $1, 2, ..., n - 1$ electrons. This is proven in the same way as eq. (7) [+7].

[+7] This attractive intuition can be used as the basis for a *proof* of eq. (7); see ref. [20] or ref. [19], § XIII.5.

[+8] That Σ has this form depends on the fact that W is a *repulsive Coulomb* potential. Otherwise [18], the description is more complicated.

(iii) If ϕ is $U_{R_0}(\theta)$ analytic, then $(\phi, (H_{R_0}(\theta) - z)^{-1}\phi)$ can be continued in the usual way. Because the set $\mathcal{U}$ described above is dense in the U_{R_0} analytic vectors, one can show that E is a discrete eigenvalue of $H_{R_0}(\theta)$ if and only if it occurs as the pole of some $(\phi, (H_{R_0}(\theta) - z)^{-1}\psi)$ for some ψ, ϕ in $\mathcal{U}$. Since $\mathcal{U}$ is independent of R_0, this has the important consequences that *the positions of resonances are independent of R_0* so long as one runs through permissible R_0 and in particular, if V is dilation analytic in the usual sense, the positions coincide with those in the Balslev–Combes theory.

In this way one has a framework for defining resonance BO curves [+9,10]. This procedure is clearly *not* as convenient as in the atomic case where the same matrix elements needed for bound-state calculations can be used for resonance calculations; indeed, it is clear that one needs some considerable thought before attempting calculations in our framework. We had originally hoped that we would find a justification for the calculational procedure suggested by McCurdy and Reseigno [15]. It does not appear that we succeeded on that account. It remains to be seen whether some synthesis is possible which retains the firm mathematical basis of our approach and the calculational convenience of the approach of McCardy and Reseigno.

[+9] Of course, as the nuclear separation changes, we have to change R_0 but by the independence of the curves on permissible R_0, this does not matter.

[+10] The framework also implies a number of other results, all familiar in the Balslev–Combes framework, e.g. convergence of time-dependent perturbation theory.

References

[1] G. Gamow, Constitution of atomic nuclei and radioactivity (Oxford U.P., 1931); Siegert, Phys. Rev. 56 (1939) 750.

[2] A. Bottino, A.M. Longoni and T.Regge, Nuovo Cimento 23 (1962) 954.

[3] C. Lovelace, in: Strong interactions and high energy physics, ed. R.C. Moorehouse (Oliver and Boyd, London, 1964).

[4] J.M. Combes, unpublished manuscript (1970).

[5] J. Aguilar and J. Combes, Commun. Math. Phys. 22 (1971) 269;
E. Balslev and J. Combes, Commun. Math. Phys. 22 (1971) 280.

[6] C. van Winter, J. Math. Anal. Appl. 47 (1974) 633; 48 (1974) 368; 49 (1975) 88.

[7] B. Simon, Commun. Math. Phys. 27 (1972) 1.

[8] B. Simon, Ann. Math. 97 (1973) 247.

[9] B. Peart and K. Dolder, J. Phys. B6 (1973) 1497.

[10] G. Doolen, Phys. Rev. A12 (1975) 1121.

[11] B. Simon, Int. J. Quantum Chem. 14 (1978) 529.

[12] W. Hunziker, in: The Schrödinger equation, eds. W. Thirring and D. Urban (Springer, 1977).

[13] W. Reinhardt, Phys. Rev. 15A (1977) 832.

[14] There is a large literature on calculations based on this method; see e.g., Proc. 1977 Sanibal Workshop on Complex scaling, Int. J. Quantum Chem. 14 (1978), special issue, to be published.

[15] C.W. McCurdy and T.N. Rescigno, Phys. Rev. Lett. 41 (1978) 1364.

[16] W. Reinhardt, Int. J. Quantum Chem. Symp. 10 (1976) 359.

[17] I. Herbst, Commun. Math. Phys., to be published;
S. Graffi and V. Greechi, Commun. Math. Phys. 62 (1978) 83;
see also I. Herbst and B. Simon, Phys. Rev. Lett. 41 (1978) 67.

[18] B. Simon, Exterior complex scaling and molecular resonances in the Born–Oppenheimer approximation, in preparation, to be submitted to Ann. Phys.

[19] See M. Reed and B. Simon, Methods of modern mathematical physics IV, analysis of operators (Academic Press, 1978) for technical terminology.

[20] V. Enss, Commun. Math. Phys. 52 (1977) 233.