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Streamlined eigenchannel treatment of open-shell spectra

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An energy-independent transformation of the generalized eigensystem used in eigenchannel calculations is shown to give the energy dependence of the R matrix in semianalytic form. The transformation gives insight into the energy dependence of the short-range parameters used in multichannel quantum-defect theory. We present a simple method for setting up the many-electron basis set which integrates naturally with the noniterative eigenchannel method. The approach is used to calculate energy-dependent quantum defects for the ${}^1S^e$ and ${}^3P^e$ symmetries of silicon near the first ionization threshold, with spin-orbit effects described by a frame transformation.

The utility of R-matrix methods for calculating open-shell spectra has been clearly demonstrated.[1-3] Especially when combined with multichannel quantum-defect techniques (MQDT),[4-6] an efficient and compact description of bound, continuum, and autoionizing spectra is obtained. Its efficiency derives from the concentration of computational effort at small distances ($r<r_0\approx 15$ a.u. for most atoms near the lower ionization thresholds), which is precisely where the difficult electron-electron correlation effects dominate. The often-complicated spectral manifestations of electron escape to larger radii (in a Rydberg or continuum state) are described in semianalytic fashion by MQDT.

The Wigner-Eisenbud[7] formulation of R-matrix methods has been widely used in atomic and molecular applications. Developed into a large-scale computational package by Berrington and co-workers,[8] it has been successfully applied to a wide range of atomic spectra. The eigenchannel R-matrix method is an alternative approach proposed initially by Fano and Lee.[9] A noniterative reformulation[10,11] based on a direct variational expression for the logarithmic derivative of the many-electron wave function on the reaction surface ($r_{\max}=r_0$) greatly improves the efficiency of the Fano-Lee treatment. This has been demonstrated through numerous applications in the last few years to alkaline-earth atoms[12,13] and to aluminum.[14]

In this Rapid Communication, we point out a further transformation of the generalized eigenvalue problem that is solved in the noniterative eigenchannel method as a function of the total energy E. In this new transformed representation, the dimension of the final generalized eigenvalue problem is of the order of *the number (N) of open or weakly closed channels* used in the calculation. This speeds up the energy-dependent calculation immeasurably, considering that previously the dimension of the eigensystem solved at each E was the total number (n_{CFG}) of antisymmetric many-electron configurations — frequently two orders of magnitude larger than N in an open-shell atom.

The determination of the matrix needed to accomplish this transformation still involves diagonalization of a large Hamiltonian matrix (roughly of order $n_{\text{CFG}}\times n_{\text{CFG}}$), but this large diagonalization now needs to be performed only once. In other words, this transformation essentially gives the energy dependence of the R-matrix eigenvalues and eigenvectors in semianalytic form. The desired short-range MQDT parameters can now be easily and rapidly calculated on as fine an energy mesh as desired, and the faster convergence[10,15] of the eigenchannel R-matrix method is still retained without use of a "Buttle correction."

The eigenchannel treatment starts from a variational expression for the logarithmic derivitive of the many-electron wave function at the surface S enclosing a reaction volume V in *configuration space.*[10,11] Out of a set of degenerate multichannel states at the energy E, the eigenchannel method selects a set of states ψ_β, orthogonal over S, each of whose normal logarithmic derivatives $-b_\beta\equiv[\psi_\beta^{-1}(\partial\psi_\beta/\partial n)]_S$ is constant across the reaction surface. These $(-b_\beta)$ are the reciprocal eigenvalues of the R matrix. For the purposes of this paper, the reaction volume V is the set of all points in configuration space for which *each* electron lies within a sphere of radius r_0. For a many-electron atom, V has the shape of a hypercube whose axes are the radial distances r_i of each electron from the nucleus.

A convenient form normally used for the trial solution is a linear combination of known functions y_k with unknown coefficients of superposition, i.e., $\psi_\beta=\sum_k y_k Z_{k\beta}$. This trial solution leads to a generalized linear eigensystem determining each coefficient vector $\mathbf{Z}$ and its corresponding eigenvalue b

$$\underline{\Gamma}\mathbf{Z}=b\underline{\Lambda}\mathbf{Z}\,, \tag{1}$$

with

$$\Gamma_{kk'}=2\int_V y_k^*(E-H)y_{k'}dV-\int_S y_k^*\frac{\partial y_{k'}}{\partial n}dS\,, \tag{2a}$$

and

$$\Lambda_{kk'}=\int_S y_k^* y_{k'}dS\,. \tag{2b}$$

In Eq. (2a) H is the Hamiltonian. This system of equations must be solved numerically for each energy E at which the R matrix is desired.

In previous eigenchannel studies[12–15] the y_k have been chosen as antisymmetrized Slater-determinantal basis functions (with definite L, S, and parity) composed of one-electron orbitals $R_{nl}(r)Y_{lm}(\theta,\phi)$. The $R_{nl}(r)$ are eigenfunctions of a radial Schrödinger equation with a numerical potential of the Hartree-Slater type. This choice of basis functions would be quite similar to that used in any standard configuration-interaction (CI) calculation, except that Refs. 12–15 use two distinct types of one-electron radial orbitals. *Closed-type orbitals* $R_{n_c l}$ are chosen to be eigenfunctions that *vanish* at $r=r_0$, while *open-type orbitals* $\bar{R}_{n_o l}(r)$ are *nonzero* at $r=r_0$. The $R_{n_c l}(r)$ are automatically orthogonal but they are not orthogonal to the open-type orbitals. For convenience in calculating interaction matrix elements (of $1/r_{ij}$), we assume further that the open-type $\bar{R}_{n_o l}(r)$ are next Gram-Schmidt-orthogonalized to the $R_{n_c l}$ and to each other, giving a new orthonormal set $\{R_{n_c l}, R_{n_o l}\}$.

As currently formulated, these R-matrix and MQDT technologies are only capable of dealing with escape of *one* electron from the reaction volume V. Because of this, we similarly group the many-electron basis functions y_k into open-type and closed-type sets. Each many-electron basis function y_k^c of the closed-type set is constructed using only closed-type one-electron orbitals, whereby y_k^c vanishes on S. Each antisymmetric basis function y_k^o of the open-type set is nonzero on S, and is built from an open-type orbital for *one* of the electrons, with all the remaining electrons placed in closed-type orbitals. It is these open-type basis functions y_k^o which allow the outermost electron to reach the reaction surface, and to escape beyond it in an excited bound or continuum state. The specification of the open-type basis set is discussed further below.

In a partitioned matrix notation referring to these closed and open basis sets, we use the fact that $\underline{\Lambda}^{cc}=0$, $\underline{\Lambda}^{co}=0$, $\underline{\Lambda}^{oc}=0$, and $\underline{L}^{cc}=0$ to rewrite Eq. (1)

$$(E\underline{I}-\underline{H}^{cc})\mathbf{Z}^c-(\underline{H}^{co}+\underline{L}^{co})\mathbf{Z}^o=0\,, \tag{3a}$$

$$-2(\underline{H}^{oc}+\underline{L}^{oc})\mathbf{Z}^c-2(\underline{H}^{oo}+\underline{L}^{oo}-E\underline{I})\mathbf{Z}^o=b\underline{\Lambda}^{oo}\mathbf{Z}^o\,. \tag{3b}$$

Here $\underline{L}$ denotes the matrix of the Bloch operator in Eq. (2a), namely $L_{kk'}=\frac{1}{2}\int_S y_k^*(\partial y_{k'}/\partial n)dS$. The matrix $\underline{L}^{co}$ also vanishes but has been retained in (3a), nevertheless, as a reminder that $\underline{H}+\underline{L}$ is a Hermitian operator. [Also, in contrast to earlier eigenchannel studies using nonorthogonal basis sets, Eqs. (3) assume the entire basis to be orthogonal. Extension of the present analysis to nonorthogonal bases is quite straightforward.] The unit matrix is denoted $\underline{I}$. Using (3a) to eliminate $\mathbf{Z}^c$ from (3b), the equation determining the eigenvalues b is now of much smaller dimension

$$\underline{\Omega}\mathbf{Z}^o=b\underline{\Lambda}^{oo}\mathbf{Z}^o\,, \tag{4}$$

where

$$\underline{\Omega}=-2(\underline{H}^{oc}+\underline{L}^{oc})(E\underline{I}-\underline{H}^{cc})^{-1}(\underline{H}^{co}+\underline{L}^{co})$$
$$-2(\underline{H}^{oo}+\underline{L}^{oo}-E\underline{I})\,.$$

These equations can now be transformed into a form more efficient for numerical solution. The idea is simply to transform this basis set into a representation in which the *closed-portion* of the Hamiltonian matrix $\underline{H}^{cc}$ is diagonal with energy eigenvalues E_λ, using an orthogonal eigenvector matrix $X_{k\lambda}$. This permits the matrix $\underline{H}^{cc}-E\underline{I}$ to be efficiently inverted as a function of E. The matrix Ω in Eq. (4) is then explicitly

$$\Omega_{kk'}=-2\sum_\lambda\frac{(\bar{\underline{H}}^{oc}+\bar{\underline{L}}^{oc})_{k\lambda}(\bar{\underline{H}}^{co}+\bar{\underline{L}}^{co})_{\lambda k'}}{E-E_\lambda}$$
$$+2E\delta_{kk'}-2(\underline{H}^{oo}+\underline{L}^{oo})_{kk'}\,. \tag{5}$$

The notation $\bar{\underline{H}}^{oc}$ implies that the matrix $\underline{H}^{oc}$ has been transformed into the representation in which $\underline{H}^{cc}$ is diagonal, e.g., $\bar{\underline{H}}^{oc}=\underline{H}^{oc}\underline{X}$.

The point of this paper is that the much smaller eigensystem (5) can be solved in a negligible amount of time on an arbitrary energy mesh using the transformed representation for $\underline{\Omega}$ in Eq. (5). To ensure that the proper number of nontrivial eigenvalues b_β is obtained (for an N-channel calculation we require N such eigenvalues), the design of the open-type basis set is important. When dealing with multiconfiguration ionic core states in particular, this will be achieved if each open-type basis function y_k^o includes a full (antisymmetric) multiconfiguration eigenstate Φ_i of the "target" Hamiltonian having one fewer electron. In this notation Φ_i is understood to include also the angular and spin-wave functions of the outermost electron coupled to form a definite L and S. It thus represents a standard "channel function" (or "surface harmonic")[10] of the type used in MQDT or close-coupling descriptions. Hence, the form we adopt for the antisymmetric open-type basis functions is $y_k^o=\mathcal{A}\{\Phi_i R_{n_o l_i}\}$, where $\mathcal{A}$ is an antisymmetrization operator.

In practice the inclusion of two such open-type basis functions $\{n_o\}$ for each channel $\{i\}$ seems to give good results, although there is considerable flexibility. When a large number of them are included in any channel it can be counterproductive as it eventually causes linear dependence difficulties, but this should never be necessary. The reason such a small number of open-type basis functions is needed seems to derive from the fact that the set of closed-type basis functions alone forms a complete orthonormal set of eigenfunctions which spans the reaction volume. However, this closed-type basis set would only be efficient for describing a solution of the Schrödinger equation which also vanishes on the reaction surface S ($r_{\max}=r_0$). By including a small additional open-type basis the entire set is made "overcomplete" (prior to its truncation), thereby giving precisely the flexibility needed to represent any continuum state having an arbitrary logarithmic derivative on the reaction surface. Accordingly the final dimension of the generalized eigensystem (4) is roughly $2N$, with N the number of open or weakly closed channels to be included in the subsequent MQDT calculation.

This choice of the open-type basis now guarantees that the solution of Eq. (4) will produce exactly N nontrivial eigensolutions because the structure of the matrix $\underline{\Lambda}^{oo}$ is block diagonal in the channel index i, with each block separable

$$\Lambda^{oo}_{kk'} = r_0^2 R_{n_o l_i}(r_0) R_{n_o' l_i}(r_0) \delta_{ii'} . \tag{6}$$

(Recall that for open channels the subscript k actually refers to both the channel subscript i and to the "open-orbital" subscript n_o.) Also, by choosing the open-type basis in this fashion, the R-matrix eigenvector corresponding to the eigenvalue b_β is now given in terms of the eigenvector of Eq. (4) by

$$W_{i\beta} = \sum_{n_o} r_0 R_{n_o l_i}(r_0) Z^o_{in_o,\beta} . \tag{7}$$

Upon normalizing the column vectors comprising the matrix $W_{i\beta}$ to unit norm, this collection of real eigenvectors forms an orthogonal matrix. This information suffices to construct the smooth, short-range-reaction matrix $\underline{K}$ used in quantum-defect studies.[12-15]

To assess this design of the many-electron variational basis set we have calculated energy-dependent single-channel quantum defects for $^1S^e$ and $^3P^e$ symmetries of silicon from the Si ground-state energy up to the lowest ionization threshold. As in our earlier calculations[13] we use a Hartree-Slater potential with a small empirical polarization correction optimized to describe accurately the e-Si^{4+} interaction. The polarization correction term includes an l-dependent "cutoff radius" chosen to give good agreement with the one-electron energy levels of Si^{3+}. Using this model Hamiltonian, we first calculate a CI ground state for Si$^+$ inside our R-matrix box of radius $r_0 = 9$ a.u. by diagonalizing the three-electron Hamiltonian in a basis of 18 closed-type basis functions. Next we set up a similar basis of closed-type (symmetry-adapted) single-configuration states such as $3s^2 3p^2$, $3s^2 3p4p$, $3p^4$, etc. To test convergence we used anywhere from 80 to 200 such single-configuration states, giving nearly identical results. The final results presented here are from our largest calculation with ≈ 200 closed-type four-electron basis functions. Lastly the "open portion" of our basis set involves two multiconfiguration open-type states of the type y^o_k defined above, each of which uses our finite-volume CI wave function for the Si$^+$ ground state. Matrix elements of the four-electron Hamiltonian were then calculated according to the CI formulation of Fano.[16] The resulting LS-coupled quantum defects are seen in Fig. 1 to vary strongly with energy, even though there are no bound perturbing configurations for these two symmetries.

These LS-coupled quantum defects could be compared directly with experimental quantum defects far below the Si$^+(3s^2 3p)$ threshold, but closer to threshold the $3p_{1/2} - 3p_{3/2}$ spin-orbit splitting mixes the two LS-coupled series of Si Rydberg levels. Hence, we apply a standard LS-jj recoupling transformation which combines the $^3P^e$

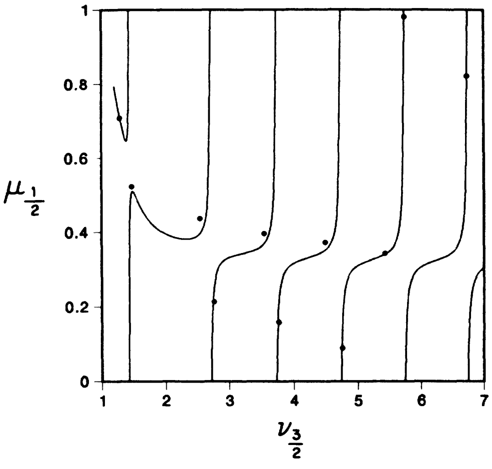

FIG. 2. Extended Lu-Fano plot of $J = 0$ even-parity bound levels of silicon. The horizontal axis shows the effective quantum number $\nu_{3/2}$ in the upper fine-structure channel $3s^2 3p_{3/2} \epsilon p_{3/2}$, while the vertical axis gives the quantum defect relative to the lower channel $3s^2 3p_{1/2} \epsilon p_{1/2}$. Solid dots show experimental levels from Ref. 18 and the curve represents the present calculation. Note that the plot is not periodic in $\nu_{3/2}$ owing to the energy-dependence of the eigenquantum defects in Fig. 1.

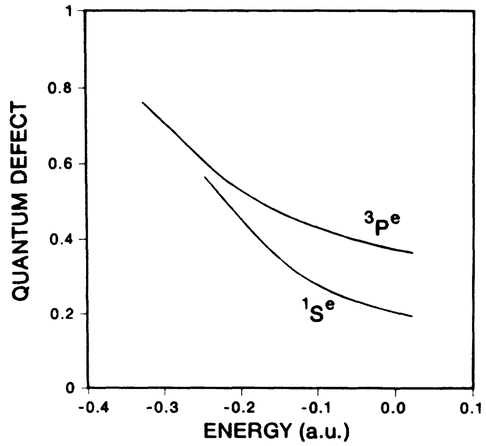

FIG. 1. Single-channel eigenquantum defects for $J = 0$ even-parity levels of silicon are shown as functions of energy relative to the lowest ionization threshold, as calculated in LS coupling.

TABLE I. Effective quantum numbers of $J = 0$ even-parity levels of Si in the lowest ionization channel ($j_i = \frac{1}{2}$).

Designation of Ref. 18	$\nu_{1/2}$(calc.)	$\nu_{1/2}$(expt.[a])
$3s^2 3p^2\ ^3P$	1.287	1.292
$3s^2 3p^2\ ^1S$	1.489	1.476
$3s^2 3p4p\ ^3P$	2.594	2.562
$3s^2 3p4p\ ^1S$	2.775	2.786
$3s^2 3p5p\ ^3P$	3.625	3.603
$3s^2 3p5p\ ^1S$	3.831	3.842
$3s^2 3p_{1/2} 6p_{1/2}$	4.645	4.627
$3s^2 3p_{3/2} 6p_{3/2}$	4.902	4.911
$3s^2 3p_{1/2} 7p_{1/2}$	5.659	5.657
$3s^2 3p_{3/2} 7p_{3/2}$	6.013	6.019
$3s^2 3p_{1/2} 8p_{1/2}$	6.671	
$3s^2 3p_{3/2} 8p_{3/2}$	7.178	7.179
$3s^2 3p_{1/2} 9p_{1/2}$	7.683	
$3s^2 3p_{3/2} 9p_{3/2}$	8.405	

[a] Reference 18.

and $^1S^e$ quantum defects into a 2×2 reaction matrix in jj coupling.[5,17] Then using the experimental fine-structure splitting of the Si^+ thresholds, the standard formulas of MQDT can be used to construct the Lu-Fano-type diagram[5,17] of $J=0$ even-parity levels of Si shown in Fig. 2.

The favorable comparison between experimental[18] and calculated quantum defects in Fig. 2 shows that a relatively small-scale eigenchannel R-matrix calculation can be used to predict nontrivial spectroscopic details of an open-shell atom as complicated as Si. Table I permits a more detailed comparison. (Effective quantum numbers predicted by a Hartree-Fock calculation are 1.33 and 1.64 for the lowest $^3P^e$ and $^1S^e$ levels in Table I, respectively.)

These results suggest that similar analyses may be useful for comparison with the detailed semiempirical MQDT studies carried out by Ginter and Ginter for Si and other atoms of the carbon group.[19] They may also serve as a starting point for the analysis of spectra in far more complex systems. The transformation described in the present paper improves considerably the efficiency of this framework.

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