Q-Chem: an engine for innovation

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Q-Chem is a general-purpose electronic structure package featuring a variety of established and new methods implemented using innovative algorithms that enable fast calculations of large systems on regular laboratory workstations using density functional and wave-function-based approaches. It features an integrated graphical interface and input generator, a large selection of functionals and correlation approaches including methods for electronically excited states and open-shell systems. In addition to serving the computational chemistry community, Q-Chem also provides an excellent development platform. © 2012 John Wiley & Sons, Ltd.

QUANTUM CHEMISTRY

'To understand something means to derive it from quantum mechanics that nobody understands.' – *Anonymous*

Quantum mechanics (QM) provides fundamental laws governing properties of matter on the atomic scale. $\hat{H}$, the Hamiltonian, defines the system (the number of nuclei and electrons and their interactions with each other and external potentials), and Ψ, the wave function, has all the answers. By solving the Schrödinger equation, $\hat{H}\Psi = E\Psi$, one can find equilibrium structures of molecules and materials, compute all sorts of spectra, and calculate thermochemical quantities that determine reaction rates and yields. Thus, as eloquently pointed out by Dirac in 1929, the laws determining all of chemistry (and a large part of physics) are completely known. Yet, the practical application of these laws is limited by the computationally demanding nature of the underlying equations. Developing approximate practical methods for applying QM to describe matter is what defines the field of quantum chemistry. Advances in computer technology, together with progress in developing efficient approximate methods and computer codes for solving the Schrödinger equation, have made quantum chem-

istry tools indispensable in modern research. The role of quantum chemistry was recognized by the award of the Nobel Prize in Chemistry to John Pople and Walter Kohn for pioneering contributions in developing methods that can be used for theoretical studies of the properties of molecules and the chemical processes in which they are involved.

Because of its pragmatic nature, quantum chemistry requires an engine, a computer program that allows one to solve the Schrödinger equation for specific systems. Today, quantum chemistry is powered by several software packages, some of them highlighted in these series, that include a variety of established and new electronic structure methods and are constantly being modified to keep up with changing computer architectures and advances in computational algorithms. This paper focuses on the Q-Chem electronic structure program. We begin with a brief history of Q-Chem and survey its capabilities, highlighting recent developments. For a more detailed technical description, interested readers are referred to the papers reviewing Q-Chem's features,[1,2] the current Q-Chem manual (www.q-chem.com), and general reviews on *ab initio* methodology.[3,4]

Q-CHEM: A BRIEF HISTORY

Q-Chem Inc. is a software company that was based in Pittsburgh, in the United States, for many years, but which will relocate to California in 2013. It was founded in 1993 as a result of disagreements within the Gaussian company that led to the departure (and

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len[0]              length of uncontracted u-array [e0|f0]
len[1]              length of contracted c-arrays
len[2]              number of c-arrays (nccc)
len[3]              space for prih2 increment instructions
len[4]              space for prih2 deblock instructions
len[5]              number of subquartets (nsubq)
      Note:  Batch size N assumed to be 1 in this version
*               PMWG  (12/94)                              *
*               JAP   (12/02)                              *
*********************************************************************/
int i,j,k,l,kk,ib,sc;
int pt[10];
// cout<<"inside new jpprih12 len012 "<<len[0]<<' '<<len[1]<<' '<<len[2]<<endl;
// cout<<"Enter jpprih12 with N KKet KBra "<<N<<' '<<KKet<<' '<<KBra<<endl;
int KLL = nd*300 + (*LBra)*10 + *LKet;
      // Gather the PA and QC arrays...
jpprehla (pa,qc,p,q,&KBra,&KKet,&NumIJ,&NumKL,&KLL);
int NKK = N * KKet * KBra;
int LTot = *LBra + *LKet + nd;
      // The arrays z,r,pa,qc must be transposed into zz,rr,pp,qq:
for (i=k=0;i<NKK;++i)
 for (j=0;j<LTot+1;++j,++k) zz[k] = z[NKK*j+i];
for (i=k=0;i<NKK;++i)
 for (j=0;j<6;++j,++k) rr[k] = r[NKK*j+i];
for (i=k=0;i<NKK;++i)
 for (j=0;j<4;++j,++k) pp[k] = pa[NKK*j+i];
for (i=k=0;i<NKK;++i)
```

FIGURE 1 | A snapshot of the code submitted by John Pople to Q-Chem in August 2003. Written elegantly in C++, it significantly improves the efficiency of the original Head–Gordon–Pople integral code in Q-Chem and speeds up Hartree–Fock and hybrid density functional theory calculations.

subsequent 'banning') of John Pople and a number of his students and postdocs.[5,6]

The first lines of the Q-Chem code were written by Peter Gill, at that time a postdoc of Pople, during a Christmas vacation (December 1992) in Australia. Gill was soon joined by Benny Johnson (a Pople graduate student) and Carlos Gonzalez (another Pople postdoc), but the latter sold his interest in the company shortly thereafter. In mid-1993, Martin Head-Gordon, formerly a Pople student but at that time on the Berkeley tenure track, joined the growing team of academic developers.

After hiring Eugene Fleischmann as a marketing director, the company acquired its URL (www.q-chem.com) in January 1997 and released its first commercial product, Q-Chem 1.0, in March 1997. Although advertising postcards celebrated this with the proud headline that 'Problems which were once impossible are now routine', version 1.0 had many shortcomings and a wit once noted that the words 'impossible' and 'routine' should probably be interchanged! However, notwithstanding the inevitable teething problems of infancy, vigorous code development ensured that, by the following year, Q-Chem 1.1 offered most of the basic quantum chemical functionality as well as a growing list of features (the continuous fast multipole method[7], J-matrix engine[8], COLD PRISM for integrals[9], and G96 density functional[10], for example) that were not available in any other package.

Following a set-back when Johnson left, the company became more decentralized, establishing relationships with an ever-widening circle of research groups in universities around the world. In 1998, Fritz Schaefer accepted an invitation to join the Board of Directors and, early in 1999, as soon as his non-compete agreement with Gaussian had expired, John Pople joined as both a Director and a code developer. Until his death, he was actively involved in shaping Q-Chem's goals and was working on improving methods and algorithms. He was particularly interested in schemes for accelerating the computation of two-electron integrals, and a snippet of his code is shown in Figure 1.

A fruitful collaboration with Wavefunction Inc. began in 2000 and led to the incorporation of Q-Chem as the *ab initio* engine in all modern versions of the Spartan package. The Board was expanded in March 2003 with the addition of Anna Krylov (University of Southern California) and the promotion of Jing Kong (who had joined the company as a postdoc seven years earlier). In 2012, Schaefer became a Board Member Emeritus, Kong became a Q-Chem Fellow, and John Herbert (Ohio State University) joined the Board. The Board of Directors currently consists of Gill (President), Krylov, Herbert, and Hilary Pople (John's daughter). Martin Head-Gordon is an invaluable Scientific Advisor to the Board.

As illustrated in Figure 2, which shows citation records for the Q-Chem 2.0 and 3.0 releases,
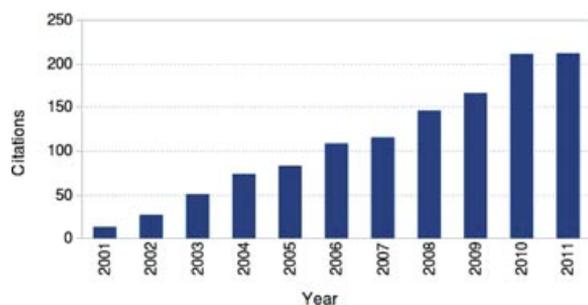
FIGURE 2 | Thousands of Q-Chem copies are being used, as estimated from the number of issued licenses. The citations of the two Q-Chem papers[1,2] has reached 200 per year in 2010, and is growing (as reported by *ISI Web of Science*). As part of the IBM World Community Grid, about 350,000 Q-Chem calculations are performed every day by the Harvard Clean Energy Project,[11] which is powered by Q-Chem, free of charge.

the package's user base is rapidly expanding. Innovative algorithms and new approaches to electronic structure have enabled cutting-edge scientific discovery and contributions from numerous scientific collaborators have facilitated the transition from an in-house code to a major electronic structure engine. Indeed, Q-Chem's most important asset is its developer base. We estimate that, since 1992, well over 300 man (and woman) years have been devoted to its code development.

Q-Chem 4.0 was released in January 2012. It consists of 3.3 million lines of code, of which 1.5 million are machine-generated, and includes contributions from more than 150 developers (the current estimate is 169).

OVERVIEW OF CAPABILITIES AND HIGHLIGHTS

Q-Chem features an extensive set of established and novel electronic structure methods, the development of new methods being driven and inspired by exciting applications. Below we provide a brief overview, with examples of applications enabled by these tools.

Self-Consistent Field and Density Functional Theory Methods

Any electronic structure calculation starts with self-consistent field (SCF) calculations, *i.e.*, solving the Hartree–Fock (HF) or Kohn–Sham equations, and fast and robust SCF algorithms are essential for practical applications. Q-Chem has a state-of-the-art integrals package, and offers dual-basis SCF (which allows one to obtain large-basis results using a fraction of the computing time[12–14]), improved integral and Fock matrix evaluation and grid techniques (e.g., an incremental SCF strategy, the Fourier-transform Coulomb method,[15,16] the MRXC scheme[17], and more), which combine to allow large systems to be studied on modest laboratory workstations, as the example in Table 1 illustrates.

Functionality is no less important than speed and Q-Chem's SCF suite offers a variety of molecular orbital guesses (including orbitals from a smaller basis set) as well as the ability to specify and maintain a desired orbital occupation via the maximum overlap method.[18,19]

Because of its computational efficiency and conceptual simplicity, density functional theory (DFT) has become a major tool in quantum chemistry.[20] Yet, there are a number of open challenges (self-interaction error, dispersion, multiconfigurational situations) that are being addressed by developing novel functionals and new flavors of DFT. Q-Chem provides access to a wide variety of functionals, from established workhorses to recent innovations. The local density approximation (LDA), generalized gradient approximations (GGAs), hybrids, double hybrids, meta- and hyper-GGAs, long-range corrected (LRC) functionals,[21–26] dispersion corrected (both the empirical-D[27] and the more rigorous XDM[28]), as well as popular Minnesota functionals[29] are available. Energies and gradients can be calculated in the ground and excited states [via time-dependent DFT (TDDFT)], as well as in problematic open-shell [via spin-flip (SF) TDDFT[30] including noncollinear formulation[31]] and charge-transfer (via frozen[32] or constrained[33] DFT) situations. Some of the most

TABLE 1 | Timings and Total Energies for Self-Consistent Field (SCF) Calculations of Lutein ($C_{40}H_{56}O_2$) with the cc-pVDZ Basis Set (868 Basis Functions) Using One Processor of a Harpertown Node (2.5 GHz)

		Hartree–Fock	B3LYP	BLYP
Q-Chem	Energy	−1697.029488	−1708.389024	−1707.449785
	# SCF cycles	8	9	10
	Timing, s	1145	1604	625

Density functional theory calculations employ the (50,194) grid.
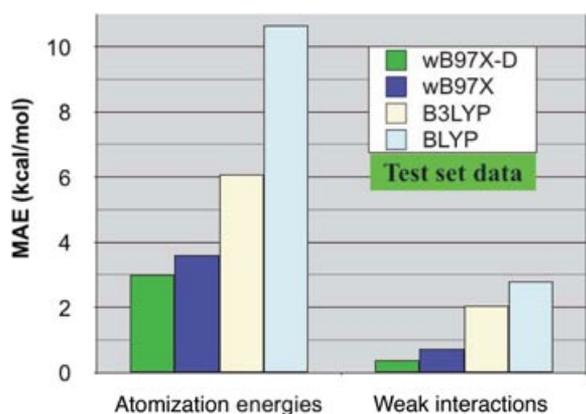
FIGURE 3 | Independent comparison of an established generalized gradient approximation (BLYP) against an established hybrid (B3LYP), a recent range-separated hybrid (ωB97X), and a range-separated hybrid that includes an empirical long-range dispersion correction (ωB97X-D). MAE (mean average errors) are computed for the atomization energies (48 reactions comprising the G3/05 test set) and weak interactions (25 intermolecular complex binding energies).[23,24]

TABLE 2 | Timings for CCSD (Coupled Cluster with Single and Double Substitutions) Energy, Properties, and Gradient Calculations for a Nucleobase Dimer ($C_9H_{10}N_8O_1$, C_1 Symmetry) with the 6-31+G(d) Basis Set (362 Basis Functions, Frozen Core, no RI). [2 $\times$ 6-core Intel Xeon node (3.06 GHz, 128 GB RAM)]

	Energy[1]	Properties[2]	Gradient[3]
1 core	101.5 h		
4 cores	26.8 h (3.8x)	31.0 h	6.4 h
8 cores	16.8 h (6.0x)	22.0 h	4.0 h

[1]CCSD equations.
[2]Λ-equations and nonrelaxed density matrices.
[3]Calculation of orbital response and relaxed density matrices.

Table 2 illustrates the parallel performance of the new CCSD code. These results are obtained using the canonical implementation and, of course, the RI variants allow access to even larger systems.

Gradients and properties calculations are implemented for a number of methods including RI-MP2, SOS-MP2, CCSD, and OO-CCD.

promising LRC functionals, which perform well for both ground-state[23,24] and excited-state[25,26] calculations, have been developed by the Q-Chem community (see Figure 3).

Accurate and Efficient Methods for Election Correlation

Theoretical model chemistries[34] based on wave function methods provide the most reliable approach to electron correlation. Q-Chem possesses highly efficient implementations of MP2 (Møller–Plesset perturbation theory) and CCSD (coupled cluster with single and double substitutions) based on dual-basis schemes[35] or density fitting.[36]

Several flavors of coupled-cluster (CC)-based methods are available: optimized-orbitals and Brueckner CCD (coupled-cluster doubles), quadratic CCD, valence optimized orbitals CCD, and a variety of perturbative higher-order corrections such as (T), (2), (dT), (fT), and so forth. All CC methods are implemented in parallel. The CC module also includes efficient use of all symmetries (permutational, spatial, and spin), active spaces, and the frozen natural orbital approach[37] for enhanced performance.

Even faster than RI-MP2 (resolution-of-identity MP2) is a new flavor of perturbation theory based on the scaled-opposite-spin idea, SOS-MP2.[38] This method shows improved performance for some problematic cases[39] and scales as N^4. Another useful perturbative model, called O2, allows the treatment of problematic open-shell situations such as spin-contaminated radicals.

Open-Shell and Electronically Excited Species

One of the distinguishing features of Q-Chem is a broad set of methods for electronically excited and open-shell species, in particular, approaches that comply with the Pople definition of a theoretical model chemistry.

As illustrated in Figure 4, equation-of-motion (EOM) CC theory,[40–42,a] EOM-CC, allows one to treat a variety of multiconfigurational wave functions within a strictly single-reference formalism. In EOM, target states Ψ_{ex} are described as excitations from a reference state Ψ_0:

$$\Psi_{ex} = \hat{R}\Psi_0 = \hat{R}e^T\Phi_0, \qquad (1)$$

where $\hat{R}$ is a general excitation operator, T is a CC operator for the reference state, and Φ_0 is the reference Slater determinant. Different EOM models are defined by choosing the reference and the form of $\hat{R}$ (Figure 4). Q-Chem features the following EOM models:[40] EOM-EE (excitation energies), EOM-IP (ionization potentials), EOM-EA (electron affinities), EOM-SF (spin-flip, for triplet and quartet references[44]), EOM-2SF (double SF, for quintet references[45]), and EOM-DIP (double IP[46]). Analytic gradients and properties are available for most of the EOM models, including such important functionality as the ability to compute transition properties between different EOM states and the calculation of Dyson orbitals.[47] In addition, an accurate
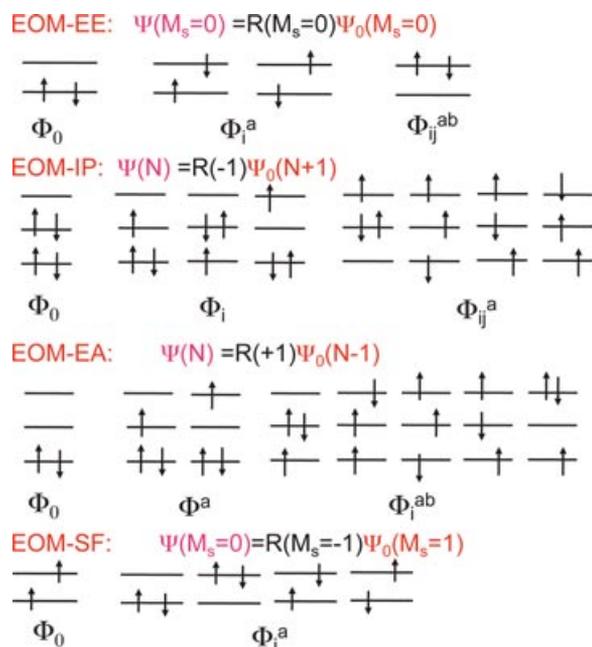
FIGURE 4 | Q-Chem includes a variety of equation-of-motion coupled-cluster (EOM-CC) methods enabling accurate calculations of electronically excited and open-shell species. In the EOM models for electronically excited states (EOM-EE, top), the reference is the closed-shell ground-state Hartree–Fock determinant (Φ_0) and the operator $\hat{R}$ conserves the number of α and β electrons generating a set of excited determinants (e.g., $\{\Phi_i^a, \Phi_{ij}^{ab}\}$ in EOM-CCSD). Nonparticle conserving and spin-flipping operators of EOM-IP/EA/SF open a route to the multiconfigurational wave functions encountered in radicals, diradicals, triradicals, and bond-breaking processes.
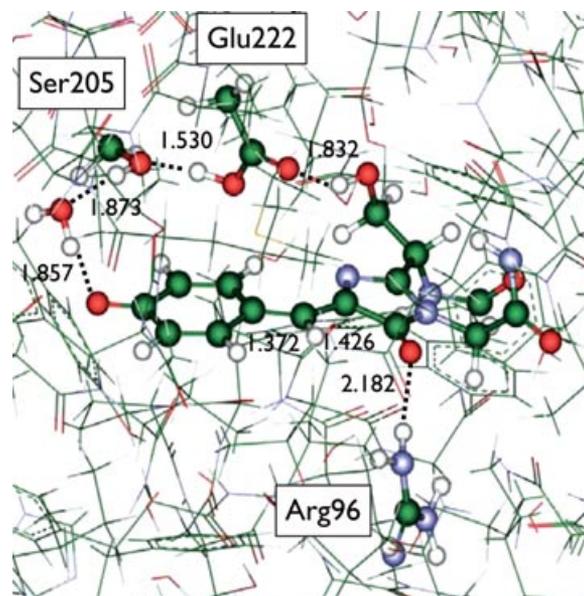

FIGURE 5 | Quantum Mechanics/Molecular Mechanics (QM/MM) calculations of optical and redox properties of the green fluorescent protein have advanced our understanding of its photophysics.[55] The chromophore and neighboring residues are included in the QM part, which can be described by DFT, SOS-CIS(D), or EOM-CCSD, whereas the rest of the protein and solvent is described by a force field.

noniterative N^7 triples correction is available for the EOM-SF and EOM-IP models.[48,49]

In addition to EOM-CC, Q-Chem also includes a similar set of methods called ADC (algebraic diagrammatic construction[50]) as well as size-intensive configuration interaction-based models (SF-CISD, IP-CISD).

Finally, there are several approximate methods that can be applied to larger molecules including RI-SOS-CIS(D) (Ref 51), an N^4 approximation to EOM-CCSD, CIS and TDDFT, SF-CIS and SF-TDDFT, and 2SF-CIS. Analytic gradients are available for many of these methods.

Methods for Large Systems: Quantum Mechanics/Molecular Mechanics and Effective Fragment Potential Methods

In addition to fast reduced-scaling algorithms, Q-Chem includes QM/MM (quantum mechanics/molecular mechanics) functionality[52] that allows one to combine a high-level *ab initio* descrip-

tion of the important part of the system while including the effect of the environment in an simplified manner, as illustrated in Figure 5. Q-Chem features the Janus interface with the YinYang atom model.[53] In addition to built-in QM/MM, Q-Chem is also integrated with Molaris, ChemShell, and CHARMM.[54]

Q-Chem also includes the effective fragment potential (EFP) method,[56–60] a nonempirical alternative to the force-field-based QM/MM. It allows one to describe systems where traditional QM/MM may be inadequate, such as chromophores with unusual electronic structure for which force-field parameters are not available, or when polarization effects are important. EFP has no empirically fitted parameters: the effective fragments' potentials are computed from *ab initio* calculations of isolated fragments. EFP has already enabled numerous computational studies of extended systems. Natural partitioning of the interaction energy into electrostatic, polarization, dispersion, and exchange-repulsion terms affords an analysis and interpretation of intermolecular forces. The EFP Hamiltonian is pairwise additive but the leading many-body effects are included through self-consistent treatment of polarization.

EFP implementation in Q-Chem features a built-in library[59] of standard fragments (e.g., common
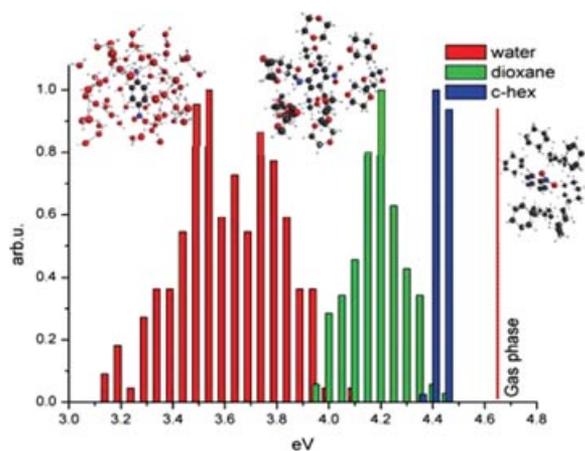
FIGURE 6 | Absorption spectra of para-nitroaniline in water, dioxane, and cyclohexane. The $\pi \to \pi^*$ state has strong charge-transfer character and large dipole moment resulting in red solvatochromatic shift in polar solvents. Accounting for solvent polarization in response to electronic excitation[58] or ionization[60] is necessary for quantitative agreement with experiment.

FIGURE 7 | Character of excited states in model systems representing green fluorescent protein (GFP) has been assigned by using attachment–detachment density analysis.[66] In particular, the attachment density allowed identification of excited states as local excitations (localized on the chromophore), or as charge-transfer-to-solvent (CTTS) ones, in which an electron is excited from the chromophore's molecular orbitals into a nearby cavity. Shown are excitation energies of a CTTS-like state [SOS-CIS(D)/6-31(2+,+)G(d,p)] and the respective attachment densities in different quantum mechanics clusters mimicking the GFP active site.[66]
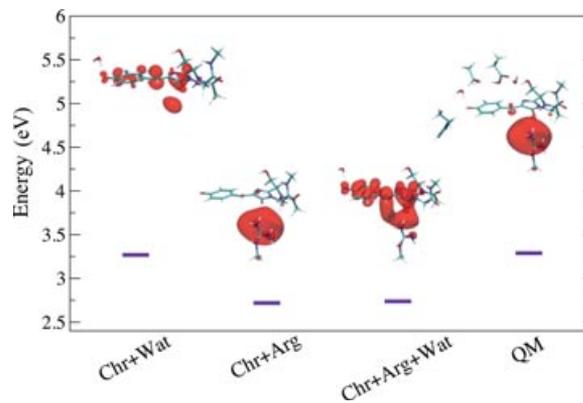
solvents, nucleobases) and is interfaced with numerous ground and excited-state methods such as DFT, TD-DFT, CIS(D), CCSD, and EOM-CCSD, which enables calculations of solvatochromic shifts (as illustrated in Fig. 6) and other types of solvent effects.

From Numbers to Insight: Visualization and Wave Function Analysis

Q-Chem 4.0 comes with the new graphical interface, IQmol,[61] written by Andrew Gilbert at the Australian National University, which includes a hierarchical input generator, a molecular builder, and general

```
void compute(btensor<4> &t2new) {

    letter a, b, c, d, i, j, k, l;

    t2new(i|j|a|b) =
i_oovv(i|j|a|b)
+ asymm(a, b, contract(c, t2(i|j|a|c), f1_vv(b|c)))
- asymm(i, j, contract(k, t2(i|k|a|b), f1_oo(j|k)))
+ 0.5 * contract(k|l, i4_oooo(i|j|k|l), t2(k|l|a|b))
+ 0.5 * contract(c|d, i_vvvv(a|b|c|d), t2(i|j|c|d))
- asymm(a, b, asymm(i, j,
contract(k|c, i1a_ovov(k|b|j|c), t2(i|k|a|c))));

    btod_delta_denom2(d_ov, 0.0).perform(t2new);
}
```

FIGURE 8 | A subroutine updating T_2 amplitudes for CCD. The contractions and other tensor operations are coded using a convenient LaTeX-style programming interface. Because low-level details are hidden, such routines are very portable, easy to read and modify. The effort required to implement new models is also significantly reduced by the interface.

visualization capabilities (MOs, molecular vibrations, etc.). In addition, Q-Chem is interfaced with WebMO and is used as the computing engine in Spartan. Other popular visualization programs such as Jmol and Molden can also be used.

In addition to visualization, wave function analysis tools are crucially important for practical applications. Q-Chem is interfaced with the Natural Bond Orbital program,[62] and includes methods such as attachment-detachment density analysis[63] (Figure 7), Boys and Edmiston-Ruedenberg localized diabatization,[64] localized orbital bonding analysis,[65] and so forth.

Tensor Library

All electronic structure equations are expressed in terms of operations between multidimensional tensors, such as one and two-electron integrals, wave-function amplitudes, and so forth. Thus, programmable expressions in wave function methods are dominated by tensor contractions (generalized matrix multiplications). The second-generation suite of CC/EOM-CC codes in Q-Chem is powered by a new C++ general-purpose library (libtensor,[67] also distributed as open source), which uses full symmetry (permutational, spatial, and spin) and has a convenient standardized interface (see Figure 8), which is flexible enough to accommodate future developments in algorithms and computational infrastructure. It is multicore parallel (see Table 2) and includes advanced memory management. The library provides an excellent environment for testing new algorithms for efficient tensor operations as well as for implementing new electronic structure models.

CONCLUSIONS AND OUTLOOK

Algorithmic and methodological challenges posed by quantum chemistry have been providing inspiration to several generations of scientists. Today's *ab initio* method-development community is vibrant and diverse, comprising groups of various sizes that are self-organized around a particular platform. The existing packages feature a variety of approaches to software development, ranging from experimental toy codes that provide a playground for testing new ideas to black-box chemistry codes targeting bench chemists and large-scale applications. Q-Chem is pursuing both of these goals, striving to bring robust, fast, and accurate tools to the scientific community while providing strong support for method developers. These two goals are synergistic: while users benefit from the latest methods and algorithms, developers maximize the impact of their research by bringing new methods to a broad community of users. However, they also pose the challenge of maintaining a robust code while enabling and facilitating experimentation. Q-Chem continues to cultivate close relationships with major research universities and to develop and maintain an infrastructure for scientific contributors. Among recent educational initiatives are user and developer workshops.

Q-Chem welcomes new contributors and recognizes intellectual contributions through acknowledgments on the Web site and inclusion on the author list of the Q-Chem papers, and also distributes more than 15% of its income as royalties. Q-Chem defines its genre as open teamware. Unlike proprietary software, the Q-Chem source code is open to a large group developers (currently more than 100 individuals in 9 countries) who can submit their contributions for inclusion in the official releases as long as they do not violate the integrity of the overall package and are scientifically sound. In addition, some of the Q-Chem modules are distributed as open source.[61,67]

NOTES

[a]Closely related to EOM-CC and linear response CC approaches are the symmetry-adapted cluster CI methods.[43]

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