Introduction
Response theory allows for the modeling of a molecular system’s response to external stimuli, and accurate ways of modeling this response are paramount to validating theory and simulations. Response to external stimuli is exactly what experimentalists measure in their labs. Thus response theory is the concrete link between theory and experiment, where direct comparison between theoretical results and experimental results can be realized.

Response Equations
The time-dependent Hartree-Fock equation, an approximation to the time-dependent Schrödinger equation, can be written in its density matrix form[1] as: \( F\rho - \hat{\rho} \beta = \beta \frac{\partial}{\partial t} \beta \). This equation can be transformed into the coupled linear response equations via perturbation theory.

\[
(1 - \beta \hat{\rho}) \left[ \left( \rho_0 - \epsilon_0 \right) \chi_p (r) + \Gamma_p (r) \right] = \omega \chi_p (r) \\
(1 - \beta \hat{\rho}) \left[ \left( \rho_0 - \epsilon_0 \right)^\dagger \chi_p (r) + \Gamma_p^\dagger (r) \right] = -\omega \chi_p (r)
\]

\[\Gamma_p (r) = \left( \frac{\partial \rho}{\partial \rho} \right) [\rho_r (r) \times \left( \sum_i \chi_i (r) \phi_i (r^\prime) + \sum_i \phi_i (r) \chi_i (r^\prime) \right)] \phi_p (r)\]

MADNESS
The MADNESS software stack allows for representation of functions in an adaptive basis set of Legendre polynomials and/or multiwavelets, thus limiting basis set error to a user-specified precision [2][3]. Operators have separated representations for efficient application in multiple dimensions. Fast, unitary transformation between function representations allows for a choice of the best space (real or multiwavelet) in which to compute for a given problem.

Methods
The standard method of computing response states and excitation energies is to project a trial wave function into a Gaussian basis and solve the corresponding matrix eigenvalue equation [4]. Because the basis inside MADNESS is not band-limited and can introduce noise of any frequency, we rearrange the response equations into a fixed-point integral equation. The resulting equation is then iterated to solution. This scheme is applied to a batch of small molecules.

Results

<table>
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<tr>
<th>Molecule</th>
<th>Water</th>
<th>Benzene</th>
<th>Methane</th>
<th>Nitrogen</th>
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<tbody>
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<td>State</td>
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<td>MADNESS</td>
<td>NWChem</td>
<td>MADNESS</td>
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</tbody>
</table>

![Figure 6: The energies reported here are singlet excitation energies in the Tam-Danchoff approximation of time-dependent Hartree-Fock theory. The states reported are the 5 lowest energy states found by the MADNESS solver or the NWChem solver. Dashes indicate that state was not found by that solver. NWChem calculations were done with the aug-cc-pvqz basis set.](image)

![Figure 7: Current log-log plot of number of states requested of single water molecule versus time to completion. Each calculation ran for 40 iterations, 20 at a lower accuracy followed by 20 at a higher accuracy.](image)

Conclusions
Through the application of the Green’s function operator, accurate excited states for some small molecules was observed. The timing of these calculations was reported. Future work will add in full TDHF and TDDFT theories, as well as improving on the scaling with both system size and number of excited states requested.

References